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JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*Ethylic Phenanthroxylene-acetoacetate.*

By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

In a paper entitled "Condensations of Glyoxal with Ethylic Malonate and Ethylic Acetoacetate," by Max Polonowsky (*Annalen*, **246**, 1), it is stated as a reason for undertaking the investigation that only the condensations of these esters with *mon*aldehydes and *mono*ketones have hitherto been studied. Polonowsky has evidently overlooked the fact that the condensation of a diketone—phenanthraquinone—with ethylic acetoacetate has been described by Japp and Streatfeild (Trans., 1883, 27).*

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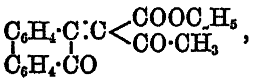
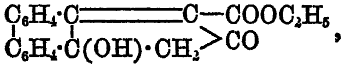
* The paper by Japp and Streatfeild was also sent—unfortunately, in English—to the *Berichte*, where a translation of it appeared (*Ber.*, **16**, 275); but this translation, which was published without being previously submitted to the authors for approval, was so disfigured by blunders (see list of errata, *Ber.*, **16**, 819), that the authors were compelled to withdraw it and to refer intending readers to the English original in the Transactions (*cf. Ber.*, **16**, 726). As a specimen of these blunders, we may mention that, in the description of the preparation of the so-called ethylic α-phenanthroxylene-isocrotonate, the words of the English manuscript, "by warming the acetic acid and zinc-dust," were transformed by the Berlin translator into "durch Erhitzen mit Zinkstaub" ("by heating with zinc-dust"), by which expression every reader would of course understand that the substance had been distilled with zinc-dust. Considering that the compound formed in this reaction was the ethyl salt of a carboxylic acid, it is not going too far to say that such a statement was calculated to raise doubts as to either the sanity or the *bona fides* of the investigators. We mention this case more particularly because, in spite of the withdrawal of the German paper, this erroneous statement as to the heating with zinc-dust has passed into the *Jahresbericht* (1883, 1011) and into Fehling's *Handwörterbuch* (**4**, 1222).

In the present paper, we describe the further investigation of ethylic phenanthroxylene-acetoacetate,



$$\begin{array}{l} C_6H_4\cdot C\!:\!C\!<\!\begin{array}{l}COOC_2H_5\\ CO\cdot CH_3\end{array},\\ \vert\qquad\ \vert \\ C_6H_4\cdot CO\end{array}$$

the condensation product obtained by the action of caustic potash on a mixture of phenanthraquinone and ethylic acetoacetate. In spite, however, of the large amount of experimental material which we have accumulated, we must reserve the detailed discussion of our results until the relation of the various compounds to one another has been more fully cleared up. For the present, we may say that the majority of these compounds appear to be derived from a compound,



$$\begin{array}{l} C_6H_4\cdot C\!=\!=\!=\!=\!=\!C\!-\!COOC_2H_5\\ \vert\qquad\ \vert \\ C_6H_4\cdot C(OH)\cdot CH_2\!>\!CO\end{array},$$

isomeric with the original condensation product, and formed from it by heating it with certain acids (concentrated formic acid, dilute sulphuric acid). This isomeride may provisionally be named *ethylic isophenanthroxylene-acetoacetate.* The above constitutional formula, which we give with reserve, represents the compound as formed by internal aldol-condensation, and accounts for the formation of a monacetyl derivative and a monohydrazone, as well as for the fact that the compound can be hydrolysed with alkalis, yielding a monobasic acid. On the other hand, the stability of this acid speaks against the formula, since a γ-ketonic acid would, in all probability, readily part with carbon dioxide, whereas this acid does not decompose below its melting point (267—269°). Moreover, the hydrazone of a γ-ketonic ester ought, under appropriate conditions, to part with alcohol, yielding a pyrazolone; but it was not found possible to effect any such transformation in the case of the hydrazone of the foregoing iso-compound.

Another result of our work is to show that two of the compounds described by Japp and Streatfeild (*loc. cit.*), namely, the so-called *ethylic α-phenanthroxylene-isocrotonate*, $C_{20}H_{16}O_3$, and the dibasic acid, $C_{16}H_{14}O_4$, are not, as was supposed, derived from the original condensation product, but, with certain modifications, from the iso-compound, and that the constitutional formulæ assigned to these compounds must, therefore, be abandoned.

By subliming the dibasic acid, $C_{16}H_{14}O_4$, Japp and Streatfeild obtained in very small quantity a compound melting at 213°, of which a single combustion, made with less than 0·07 gram, gave figures agreeing with the formula $C_{14}H_{10}O$. By employing a different method, we have obtained a better yield of this compound, and we find, both from its mode of formation and as the result of analysis, that it has the formula $C_{17}H_{12}O$.

Ethylic phenanthroxylene-acetoacetate, when heated with certain acids, undergoes a variety of chemical changes. The first observation in this direction was made in the course of an attempt to recrystallise the compound from hot glacial acetic acid, when it was noticed that an insoluble compound separated from the hot liquid in colourless, silky needles, the quantity of which increased on further boiling. This led us to examine the action of other acids, both organic and inorganic, and it was found that different acids gave different results. The action in the case of acetic acid is complex, and will be better understood when that with formic acid has first been described.

In the meantime, however, we may mention that although ethylic phenanthroxylene-acetoacetate is acted on by hot glacial acetic acid, it may be dissolved unchanged in this solvent in the cold, and we have thus been able to determine its molecular weight by Raoult's method. The result points to the formula $C_{20}H_{16}O_4$.

					Mol. wt.	
	Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$.	Depression.	Found.	$C_{20}H_{16}O_4$. Calc. for
I.	0·1716	22·35	0·7678	0·103°	290	320
II.	0·2354	25·933	0·9077	0·125	283	„

(Molecular depression of acetic acid = 39).

Action of Formic Acid on Ethylic Phenanthroxylene-acetoacetate.

The substance was heated with excess of concentrated formic acid (sp. gr. 1·22) in a sealed tube at 130° for an hour. On cooling, the greater part of the new substance was deposited in small, brownish crystals, whilst a further quantity could be precipitated from the mother liquor by the addition of water. Alcohol, benzene, light petroleum, and, finally, ethylic acetate were employed as solvents, the last-mentioned giving the best result, and depositing the compound in colourless, triclinic prisms melting at 177°. For ordinary purposes, benzene may be used as a solvent; it deposits the substance in needles, which, however, obstinately retain a trace of a pink colouring matter. This colouring matter is also formed in various other reactions here described, and greatly interferes with the purification of the products. In the case of the present compound, however, the colouring matter can be readily removed by recrystallising the substance from hot alcoholic hydrogen chloride.

Analysis gave figures which lead to the formula $C_{20}H_{16}O_4$, showing that the compound is isomeric with the original condensation product.

	Substance.	CO_2.	H_2O
I........	0·2389	0·6580	0·1075
II........	0·2378	0·6549	0·1097

	Calculated for $C_{20}H_{16}O_4$.		Found.	
			I.	II
C_{20}........	240	75·00	75·11	75·11
H_{16}	16	5·00	5·00	5·12
O_4........	64	20·00	—	—
	320	100·00		

This compound may receive the provisional name *ethylic isophenanthroxylene-acetoacetate*, but we shall also refer to it, for shortness, as the "iso-compound." We have already given the constitutional formula which we incline to assign to it.

For the following crystallographical examination of the compound we are indebted to Mr. A. E. Tutton:—

"The crystals are perfectly colourless and very highly refractive when purified by several recrystallisations from acetic ether. The reflections obtained were generally excellent; but, owing to longitudinal striation, and occasionally to the presence of twin lamellæ, recognisable by the polariscope, the prism faces often gave several images. On this account a large number of crystals were measured. They vary in size from 2 to 4 mm. in length, and from 0·5 to about 1·5 mm. in thickness.

"System: triclinic. Habit: prismatic.

"Elements. Axial angles: $\alpha = 78° 6'$, $\beta = 72° 0'$, $\gamma = 83° 18'$.
Ratio of axes: $a : b : c = 0·9640 : 1 : 0·5069$.

"Forms present: a, $\{100\}$, $\infty\bar{P}\infty$; b, $\{010\}$, $\infty\breve{P}\infty$; c, $\{001\}$, oP.
p, $\{110\}$, $\infty P'_{,}$; p', $\{1\bar{1}0\}$, $\infty{}_{,}'P$; q, $\{0\bar{1}1\}$, $'\breve{P}_{,}\infty$.

"Fig. 1 represents the usual appearance of the crystals drawn to scale, and Fig. 2 is the spherical projection.

Fig. 1.

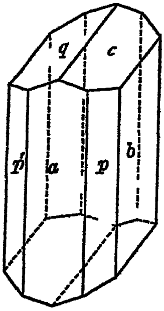
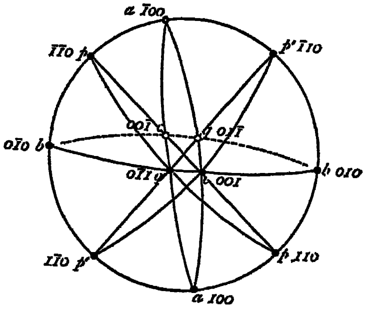


Fig. 2.



"Parallel faces *b* are generally the best developed, sometimes so much so that the crystals become converted into thin, tabular plates. All the individuals examined showed the whole six forms. Following is a table of measurements of the principal angles, together with the values obtained by calculation from the elements.

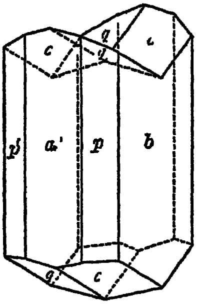
	No. of measurements.	Limits.	Mean observed angles.	Calculated angles.
$b : p$, 010 : 110	20	41° 38′—40° 18′	40° 57′	*
$p : a$, 110 : 100	20	38 30—37 14	37 53	*
$a : p'$, 100 : $1\bar{1}0$	20	49 41—47 33	48 32	48° 19′
$p' : b$, $1\bar{1}0$: $0\bar{1}0$	20	53 51—51 35	52 38	52 51
$b : c$, 010 : 001	35	75 34—74 54	75 9	*
$c : q$, 001 : $0\bar{1}1$	33	28 28—27 58	28 11	28 11
$q : b$, $0\bar{1}1$: $0\bar{1}0$	33	77 0—76 17	76 40	*
$p : c$, 110 : 001	13	67 29—66 45	67 8	67 3
$p : q$, 110 : $0\bar{1}1$	10	89 6—88 17	88 45	88 39
$a : c$, 100 : 001	14	70 23—69 41	69 57	*
$a : q$, 100 : $0\bar{1}1$	11	75 45—75 1	75 28	75 31
$p' : c$, $1\bar{1}0$: 001	11	85 26—84 44	85 8	85 13
$p' : q$, $1\bar{1}0$: $0\bar{1}1$	11	67 50—67 16	67 35	67 45

"The angles marked with an asterisk were used for the calculation of the elements. The mean temperature during the measurements was 14·8° C., the limits being 13·8—16·5°.

"There are two well-developed cleavages, one parallel to the basal plane *c*, and another parallel to the brachypinakoid *b*.

"Twins are occasionally found of the form indicated in Fig. 3.

FIG. 3.



They are produced by rotation of one individual (the front one) 180° about the vertical axis.

"The twin plane is consequently the prism zone plane, the plane of the spherical projection. The upper termination exhibits re-entrant angles, while the lower end shows apparently four pyramid faces. Measurements indicate that, as expected, the angles of the prism zone remain the same, the face $b(0\bar{1}0)$ of the front and $b(010)$ of the back crystal forming one plane in the twin. The angle made by this plane with *c* of the back crystal is 75° 9′, and with *q* of the front crystal 76° 40′. The twinning is occasionally repeated, the individuals appearing as twin lamellæ.

"As regards the optical properties, the extinctions upon all the faces are oblique to the crystallographic axes and facial edges. The extinction upon face *b* occurs at an angle of 48° to the prism edges; upon face *p*, 36°; upon *a*, 50°; and upon *c*, as seen through a cleavage plate, about 10° with the trace of *b*.

"In convergent light, looking through a cleavage plate parallel to *c* (001), one optic axis with its brush and rings is visible, emerging on the side nearest the edge *ac*, and making an apparent angle of about 46° with the normal to the plate.

"Through *b*(010) another brush is visible, the axis being apparently just beyond the edge *bp*. This axis is distinctly seen with its rings on looking through face *p*(110) near the edge *bp*. The rings are very close together even in the thinnest sections; hence the double refraction is very strong."

The same compound can be readily obtained by boiling ethylic phenanthroxylene-acetoacetate with sulphuric acid diluted with twice its weight of water. The substance cakes together to a crust, which should be broken up with a glass rod during the operation. The product was powdered under water, thoroughly washed with water, and purified as in the case of the substance obtained with formic acid. It crystallised from ethylic acetate in the prismatic forms of the iso-compound, melting, like the latter, at 177°. Analysis gave C, 74·90; H, 5·03 per cent. Calculated for $C_{20}H_{16}O_4$: C, 75·00; H, 5·00 per cent.

The crude product obtained in the foregoing reaction is yellow instead of pink, the colouring matter which gave so much trouble in preparing the compound by the action of formic acid not being formed, and the substance is consequently easier to purify.

In our first experiment with dilute sulphuric acid we obtained a practically quantitative yield of the iso-compound; but in subsequent experiments a small quantity of a substance insoluble in benzene and acetic acid was formed at the same time. This proved to be the compound $C_{20}H_{14}O_3$, more readily obtained by the action of glacial acetic acid on ethylic phenanthroxylene-acetoacetate (*vide infra*), and formed from this latter compound by elimination of a molecule of water. Possibly its formation in the present case might be avoided by the use of a more dilute sulphuric acid.

Action of Acetic Anhydride on Ethylic Isophenanthroxylene-acetate.—The iso-compound was heated with excess of acetic anhydride for three hours at 150°. As the solution, which was of a pink colour, deposited nothing on cooling, it was boiled with alcohol to destroy the excess of anhydride, and then concentrated. On cooling, large, well-shaped crystals separated, resembling in form those of copper sulphate, and melting indistinctly at 165—170°. It crystallises from benzene in thick needles. Analysis showed that a monacetyl derivative, $C_{20}H_{15}(C_2H_3O)O_4$, had been formed.

	Substance.	CO_2.	H_2O.
I........	0·1964	0·5285	0·0892
II	0·2444	0·6562	0·1113

	Calculated for $C_{20}H_{15}(C_2H_3O)O_4$.		Found.	
			I.	II.
C_{22}	264	72·93	73·38	73·22
H_{18}	18	4·97	5·04	5·06
O_5	80	22·10	—	—
	362	100·00		

The compound is identical with one of those described later, obtained by heating ethylic phenanthroxylene-acetoacetate with glacial acetic acid. On the other hand, the iso-compound does not yield this acetyl derivative when heated with glacial acetic acid, even at 150°.

Some further reactions of this acetyl derivative will be described in connection with its preparation by the second method just referred to.

Action of Phenylhydrazine on Ethylic Isophenanthroxylene-acetoacetate.—The iso-compound was heated with phenylhydrazine in alcoholic solution for an hour at 130—140°. As nothing was deposited on cooling, sufficient water was added to cause a slight turbidity, and on standing the hydrazone separated in aggregates of flat, yellow needles. The substance was recrystallised from a mixture of benzene and light petroleum, and was thus obtained as a yellow, crystalline powder. Heated in a capillary tube, it began to change colour at 140°, was quite black at 200°, and melted with strong decomposition at 210—212°. It dissolves in concentrated sulphuric acid with a deep blue colour.

Analysis of the substance dried at 100° showed that a monohydrazone, $C_{20}H_{16}O_3(N_2HC_6H_5)$, had been formed:—

I. 0·1515 gram gave 0·4245 CO_2 and 0·0737 H_2O.

II. 0·1046 „ 9·02 c.c. dry nitrogen at 16·5°, and under 522 mm. pressure. Nitric oxide absent.

	Calculated for $C_{26}H_{22}N_2O_3$.		Found.	
			I.	II.
C_{26}	312	76·10	76·41	—
H_{22}	22	5·36	5·40	—
N_2	28	6·83	—	7·01
O_3	48	11·71	—	—
	410	100·00		

The iso-compound was then heated with phenylhydrazine in alcoholic solution for two hours at 190°, in the hope that the hydrazone might split off water yielding a pyrazolone; but only the hydrazone was obtained as before.

Ethylic phenanthroxylene-acetoacetate, on the other hand, does not appear to react with phenylhydrazine under ordinary conditions: thus no action took place when the two substances were heated together in alcoholic solution for one hour at 100°. The reaction has yet to be tried at a higher temperature.

Action of Bromine on Ethylic Isophenanthroxylene-acetoacetate.—Two grams of the iso-compound were dissolved in dry chloroform, and 1 gram of bromine (also dissolved in chloroform) was added. As the colour of the bromine did not disappear, the solution was allowed to stand in a desiccator over solid paraffin. After standing for a few hours, the colour of the liquid had changed to a light yellow, and fumes of hydrobromic acid were evolved, whilst well-shaped crystals, sometimes prismatic, sometimes tabular, had separated; these were washed with chloroform and air-dried in the dark. Precisely similar crystals were obtained by further spontaneous evaporation of the mother liquors. Heated in a capillary tube, both specimens began to blacken at 195—200°, and melted with decomposition at 217°. Analysis gave results which showed that a monobromo-derivative, $C_{20}H_{15}BrO_4$, had been formed; but the carbon was found too high and the bromine too low. Calculated for $C_{20}H_{15}BrO_4$: C, 60·15; H, 3·76; Br, 20·05. Found: C, 61·27; H, 4·09; Br, 19·13. It, therefore, appeared that, in spite of its homogeneous appearance, the bromine compound was contaminated with unchanged substance.

As it was clear from the foregoing that an additive compound was not formed, we did not pursue the subject further.

Reduction of Ethylic Isophenanthroxylene-acetoacetate with Zinc and Hydrochloric Acid.—The iso-compound was dissolved in alcohol on the water-bath, and a little alcoholic hydrochloric acid and zinc filings added from time to time. After continuing the reduction for several hours, the solution was poured into water. The precipitated oily substance solidified after standing for some days, and was recrystallised from a mixture of benzene and light petroleum. The first crop of crystals melted about 165—170°, and appeared to be unchanged substance. The mother liquor deposited a substance of lower melting point: this was recrystallised from ethyl acetate, and was thus obtained in well-shaped, colourless crystals of prismatic habit, melting at 123°, and identical with the compound of the formula $C_{20}H_{16}O_3$ (m. p. 124), prepared by Japp and Streatfeild (Trans., 1883, 29) by warming the original condensation compound with hydriodic acid and amorphous phosphorus. The smallness of the yield made further purification impracticable: the compound was therefore analysed, and gave a result which, although not good, left no doubt as to the formula:—

0·1180 gram gave 0·3380 CO_2 and 0·0562 H_2O.

	Calculated for $C_{20}H_{16}O_3$		Found.
C_{20}	240	78·95	78 12
H_{16}	16	5·26	5·29
O_3	48	15·79	—
	304	100·00	

The foregoing mode of formation shows that the compound cannot well have the constitution ascribed to it by Japp and Streatfeild.

In preparing the compound by Japp and Streatfeild's method, we found it better to omit the addition of amorphous phosphorus. Ethylic phenanthroxylene-acetoacetate was boiled for a short time with fuming hydriodic acid; the product was washed with water, freed from iodine by boiling with a solution of hydrogen sodium sulphite, and recrystallised from alcohol or from a mixture of benzene and petroleum. By working in this way, the red colouring matter which gave so much trouble in the original method of preparation does not appear to be formed.

When this compound is heated with phenylhydrazine in alcoholic solution in a sealed tube at 100°, it forms a hydrazone, which separates from the hot solution as a yellow, crystalline powder, readily soluble in hot benzene, sparingly soluble in hot alcohol. For analysis it was recrystallised from a mixture of benzene and petroleum, but the recrystallisation was attended with loss, and the substance looked less pure than when merely boiled out with a little alcohol. It blackens about 190°, and is totally decomposed at 195°. A nitrogen determination showed that a monohydrazone, $C_{20}H_{16}O_2(N_2HC_6H_5)$, had been formed.

Substance.		v.	t.	p.
0·1027	dry N + NO	9·02 c.c.	17°	536 mm.
	„ N	9·02 „	17	526 „

	Calculated for $C_{20}H_{16}O_3(N_2HC_6H_5)$.	Found.
N in 100 parts	7·10	7·25

Reduction of Ethylic Isophenanthroxylene-acetoacetate with Hydriodic Acid.—The finely powdered iso-compound was heated with excess of fuming hydriodic acid in a sealed tube at 100° for 20 minutes. There was strong pressure in the tube on opening. The product was treated with water, boiled with hydrogen sodium sulphite to remove iodine, again washed, and recrystallised from boiling alcohol. It was deposited in slender, flat needles, with a brownish tinge, melting, not very sharply, at 215°. It can be obtained in *white* needles by sublimation. Analysis gave figures agreeing with the formula $C_{17}H_{12}O$:—

	Substance.	CO_2.	H_2O.
I....... .	0·0946	0·3056	0·0452
II.........	0·1055	0·3397	0·0515

	Calculated for $C_{17}H_{12}O$.		Found.	
			I.	II.
C_{17}........	204	87·93	88·10	87·81
H_{12}.......	12	5·17	5·30	5·42
O........	16	6·90	—	—
	232	100·00		

The substance is formed from the iso-compound according to the equation

$$C_{20}H_{16}O_4 + H_2 = C_{17}H_{12}O + C_2H_5{\cdot}OH + CO_2.$$

The reaction may be represented as occurring in three stages: in the first, the iso-compound is reduced to the compound $C_{20}H_{16}O_3$ (m. p. 124°):—

$$C_{17}H_{11}O_2{\cdot}COOC_2H_5 + 2H = C_{17}H_{11}O{\cdot}COOC_2H_5 + H_2O;$$

in the second, this compound is hydrolysed, yielding a monobasic acid:—

$$C_{17}H_{11}O{\cdot}COOC_2H_5 + H_2O = C_{17}H_{11}O{\cdot}COOH + C_2H_5{\cdot}OH,$$

which latter then parts with carbon dioxide:—

$$C_{17}H_{11}O{\cdot}COOH = C_{17}H_{12}O + CO_2.$$

This compound is identical with that melting at 213° obtained by Japp and Streatfeild (Trans., 1883, 33) by heating the dibasic acid $C_{18}H_{14}O_4$. On the strength of a combustion made with less than 0·07 gram they assigned to it, as already mentioned, the formula $C_{14}H_{10}O$. We have again prepared the substance by heating the dibasic acid, and find that it is indistinguishable in its physical properties from the foregoing compound obtained by the action of hydriodic acid on the iso-compound. Analysis also gave figures agreeing with the formula $C_{17}H_{12}O$, which formula, moreover, better accounts for the formation of this compound from the dibasic acid than that formerly given :—

$$C_{16}H_{12}(COOH)_2 = C_{17}H_{13}O + CO_2 + H_2O.$$

In the formation of the dibasic acid from the compound $C_{20}H_{16}O_3$ (m. p. 124°) by the action of caustic alkalis, a closed chain (probably a penta-carbon ring) is opened; in the formation of the compound $C_{17}H_{12}O$ from the dibasic acid, this ring is closed again. The compound $C_{17}H_{12}O$ is probably a ketone containing the carbonyl group in a penta-carbon ring; but its constitution has yet to be studied.

Hydrolysis of Ethylic Isophenanthroxylene-acetoacetate with Caustic Alkali.—The iso-compound dissolves readily in hot aqueous caustic soda, and from the solution hydrochloric acid precipitates the new acid as a white, crystalline powder. The yield is quantitative. It may be purified by recrystallisation either from alcohol, which deposits it in flat, satiny needles, or from glacial acetic acid, from which it separates in slender needles. It softens at 265°, and melts with decomposition at 267—269°.

Analysis gave figures agreeing with the expected formula $C_{18}H_{12}O_4$:—

0·2213 gram gave 0·6001 CO_2 and 0·0832 H_2O.

	Calculated for $C_{18}H_{12}O_4$.		Found.
C_{18}	216	73·97	73·95
H_{12}........	12	4·11	4·17
O_4	64	21·92	—
	292	100·00	

The acid has been formed by the hydrolysis of the ethyl salt, and may therefore be called *isophenanthroxylene-acetoacetic acid.*

It dissolves readily in ammonia, and from the solution barium chloride and calcium chloride precipitate gelatinous barium and calcium salts. In like manner, the silver salt was obtained as a white, apparently crystalline precipitate; it was washed with water, dried over sulphuric acid, and analysed. Different preparations did not give concordant results; but the figures left no doubt that the acid was monobasic. Calculated for $C_{18}H_{11}O_4Ag$: Ag, 27·06 per cent.

Found: 27·23 and 26·05 per cent. The carbon in both preparations was found too low, so that the salt is evidently difficult to obtain pure.

The copper salt, prepared in the same way, formed a light-green powder. For analysis it was air-dried at ordinary temperatures.

0·1562 gram, when heated at 120°, lost 0·0315 gram H_2O.

	Calculated for $(C_{18}H_{11}O_4)_2Cu + 9H_2O$.	Found.
H_2O in 100 parts	20·7	20·16

0·1227 gram anhydrous copper salt gave on ignition 0·0144 CuO.

	Calculated for $(C_{18}H_{11}O_4)_2Cu$.	Found.
Cu in 100 parts	9·77	9·35

The carbon in this specimen was 1 per cent. too high (67·94, instead of 66·93), so that this salt was also impure.

Action of Caustic Potash on Isophenanthroxylene-acetoacetic Acid.—As some of the compounds obtained from ethylic phenanthroxylene-acetoacetate are converted, by the action of caustic alkali, into salts of dibasic acids, we made an experiment for the purpose of ascertaining whether any such change could be effected in the case of isophenanthroxylene-acetoacetic acid. The reaction, however, took a wholly different course.

The acid was heated with excess of strong aqueous potash in a sealed tube at 150° for two hours. There was no pressure on opening the tube, and a solid substance had separated. The contents of the tube were poured into water, and the solid substance was separated by filtration, washed, and dried. As it was insoluble in the ordinary organic solvents of low boiling point, it was dissolved in boiling phenol, and the solution poured into hot alcohol, which caused the substance to separate almost immediately as a pale-yellow, crystalline powder. It was washed with boiling alcohol and dried for analysis. It did not melt even at 300—310°. An analysis, which had to be made with a very small quantity of substance, gave figures which agreed, although not well, with the formula $C_{17}H_{10}O$. The same substance may, however, be obtained in greater quantity by the action of acetic anhydride on isophenanthroxylene-acetoacetic acid (*vide infra*). Analyses of the substance from this source are given later on.

0·0793 gram gave 0·2563 CO_2 and 0·0348 H_2O.

	Calculated for $C_{17}H_{10}O$.		Found.
C_{17}	204	88·70	88·14
H_{10}	10	4·35	4·87
O	16	6·95	—
	230	100·00	

The substance is formed according to the equation

$$C_{18}H_{12}O_4 = C_{17}H_{10}O + CO_2 + H_2O.$$

Action of Acetic Anhydride on Isophenanthroxylene-acetoacetic Acid.—The acid was heated with acetic anhydride in a sealed tube for one hour at 150°. There was a slight pressure in the tube on opening. A substance crystallising in long, pale-yellow needles had separated; these were filtered off and thoroughly boiled with alcohol, in which they are quite insoluble. After this treatment they were washed with boiling alcohol, dried, and analysed. The compound has the formula $C_{17}H_{10}O$, and is identical with the foregoing obtained by the action of caustic potash.

	Substance.	CO_2.	H_2O.
I.......	0·2353	0·7654	0·0927
II........	0·1165	0·3776	0·0460

	Calculated for $C_{17}H_{10}O$.		Found.	
			I.	II.
C_{17}	204	88·70	88·71	88·39
H_{10}	10	4·35	4·37	4·38
O	16	6·95	—	—
	230	100·00		

The acetic anhydride mother liquor from these crystals was boiled with alcohol for some time and allowed to stand. It deposited light-brown crystals, which were purified by recrystallisation from ethylic acetate, and then formed small, transparent, pale-yellow, oblique plates melting constantly at 224—226°. At this temperature there is no decomposition, but gas is evolved on heating to 235—240°.

This compound is much more readily obtained by merely boiling isophenanthroxylene-acetoacetic acid with acetic anhydride until the insoluble compound $C_{17}H_{10}O$ begins to separate, which occurs after from 20 to 30 minutes. Alcohol is then added, and the solution is filtered hot; the filtrate deposits the new compound, which is then purified as already described. Acetic acid may also be used as a solvent, and deposits the substance in small, shining plates of the foregoing melting point.

Analysis gave figures agreeing best with the formula $C_{19}H_{14}O_4$, although the formation of a compound $C_{19}H_{16}O_4$ could be more readily accounted for.

	Substance.	CO_2.	H_2O.
I........	0·1828	0·4954	0·0815
II........	0·1842	0·5012	0·0842
III........	0·2145	0·5846	0·0910
IV........	0·2068	0·5634	0·0843

	Calc. for $C_{19}H_{14}O_4$.	Calc. for $C_{19}H_{16}O_4$.	Found.			
			I.	II.	III.	IV.
C......	74·51	74·02	73·91	74·20	74·32	74·30
H......	4·58	5·20	4·95	5·07	4·71	4·52
O......	20·91	20·78	—	—	—	—
	100·00	100·00				

Analyses I and II were made with substance recrystallised from ethyl acetate, III and IV with substance recrystallised from acetic acid.

We must leave the formula of this compound undecided for the present.

Action of Acetic Acid on Ethylic Phenanthroxylene-acetoacetate.

Three compounds are formed in this reaction.

When ethylic phenanthroxylene-acetoacetate is dissolved in glacial acetic acid and the solution boiled, slender, colourless needles speedily begin to separate from the boiling liquid. As the presence of this solid substance produced bumping, it was found more convenient to heat the ethylic phenanthroxylene-acetoacetate with acetic acid in a sealed tube at 130—140°. In this way we obtained from 5 grams of the condensation compound 1·5 grams of the new product. The mother liquor was pink-coloured.

The new compound was separated by filtration, washed with boiling acetic acid, and dried for analysis. It is practically insoluble in the ordinary organic solvents of low boiling point, but dissolves in high boiling solvents, such as phenol and ethyl benzoate, and may be precipitated in a crystalline form from these solutions by the addition of alcohol. When heated in a capillary tube it decomposes, apparently without melting, at about 285°.

It gave figures agreeing with the formula $C_{20}H_{14}O_3$, showing that it had been formed from the condensation product by the abstraction of 1 mol. of water.

	Substance.	CO_2.	H_2O.
I........	0·1897	0·5533	0·0822
II........	0·1895	0·5517	0·0827

	Calculated for $C_{20}H_{14}O_3$.		Found.	
			I.	II.
C_{20}........	240	79·47	79·55	79·40
H_{14}........	14	4·64	4·81	4·84
O_3........	48	15·89	—	—
	302	100·00		

The same compound is formed, as already mentioned, along with ethylic isophenanthroxylene-acetoacetate by the dehydrating action of sulphuric acid on ethylic phenanthroxylene-acetoacetate.

Strange to say, this abstraction of water could not be effected by boiling ethylic phenanthroxylene-acetoacetate with acetic anhydride; but by heating it in a sealed tube with the anhydride for one hour at 150°, the compound $C_{20}H_{14}O_3$, together with the compound $C_{22}H_{18}O_3$ (also formed in the acetic acid reaction, *v. infra*), was formed. A similar observation has been made by Zincke (*Ber.*, **10**, 1475), who found that water could be eliminated from benzpinacone by heating the latter with glacial acetic acid, but not with acetic anhydride.

The relation of the compound $C_{20}H_{14}O_3$ to the compound $C_{17}H_{10}O$ is perhaps expressed by the formula $C_{17}H_9O(COOC_2H_5)$; but this point requires further study. The compound is not hydrolysed by strong aqueous potash.

The acetic acid mother liquor resulting from the preparation of the compound $C_{20}H_{14}O_3$ was poured into water. A dark-red, soft substance separated which soon solidified; this was dried and treated with benzene, in which the greater part of it dissolved; the insoluble residue will be described later on. As the benzene solution, even when concentrated, did not deposit the substance in a satisfactory form, the benzene was expelled, and the residue was extracted with hot light petroleum (b. p. 90—120°) which dissolved it only sparingly, but deposited it in well-shaped crystals of a pinkish colour. After a further recrystallisation from alcohol, it was obtained colourless, and melted indistinctly at 165—171°. This substance proved to be identical with the acetyl derivative of ethylic isophenanthroxylene acetoacetate, already described. Calculated for $C_{20}H_{15}(C_2H_3O)O_4$: C, 72·93; H, 4·97 per cent. Found: C, 73·06; H, 4·91 per cent.

Boiling with aqueous caustic soda readily hydrolysed this compound and yielded a salt of isophenanthroxylene-acetoacetic acid, the acetyl group being estimated in the process. The purified acid melted at 269—270° (softening at 265°), and gave on analysis: C, 74·00; H, 4·38 per cent. Calculated for $C_{18}H_{12}O_4$: C, 73·97; H, 4·11 per cent.

The monacetyl compound was also heated in alcoholic solution with excess of phenylhydrazine at 100°. A yellow, crystalline substance separated, which was purified by dissolving it in hot benzene and pouring the solution into hot light petroleum, when it was deposited in minute, yellow needles. When heated in a capillary tube, it turned dark at about 190° and melted, with complete decomposition, about 207°. It dissolved in concentrated sulphuric acid with a dark-blue colour. It is identical with the hydrazone of ethylic isophenanthroxylene-acetoacetate already described, and is formed from the acetyl derivative with elimination of the acetyl group, doubtless according to the equation

$$C_{20}H_{15}(C_2H_3O)O_4 + 2C_6H_5{\cdot}N_2H_3 = C_{20}H_{16}O_3(N_2H{\cdot}C_6H_5) + C_2H_3O{\cdot}N_2H_2{\cdot}C_6H_5 + H_2O.$$

Calculated for $C_{20}H_{16}O_3(N_2H{\cdot}C_6H_5)$: C, 76·10; H, 5·36 per cent. Found: C, 76·76; H, 5·64 per cent. The formula

$$C_{20}H_{15}(C_2H_3O)O_3(N_2H{\cdot}C_6H_5),$$

which is that of a hydrazone formed from the acetyl compound *without* elimination of the acetyl group, would require only 74·34 per cent. of carbon.

The third compound formed by the action of acetic acid on ethylic phenanthroxylene-acetoacetate is that which is left undissolved when the substance precipitated with water is extracted with benzene. This compound is formed only in small quantity, and it was necessary to unite the products of several preparations in order to obtain enough for analysis. It was purified by recrystallisation, first from hot glacial acetic acid, afterwards from ethyl acetate, the latter solvent giving the best results. It was thus obtained in transparent, yellow, rectangular plates melting at 227°. Analysis gave figures agreeing with the formula $C_{44}H_{34}O_9$, which is that of a compound formed from 2 mols. of the foregoing monacetyl compound with elimination of 1 mol. of water:—

$$2C_{20}H_{15}(C_2H_3O)O_4 = C_{40}H_{28}(C_2H_3O)_2O_7 + H_2O.$$

This higher molecular weight is in keeping with the more sparing solubility of the compound.

0·2857 gram gave 0·7816 CO_2 and 0·1283 H_2O.

	Calculated for $C_{40}H_{28}(C_2H_3O)_2O_7$.		Found.
C_{44}	528	74·79	74·61
H_{34}	34	4·82	4·98
O_9	144	20·39	—
	706	100·00	

It is to be noted that ethylic *iso*phenanthroxylene-acetoacetate may be heated with glacial acetic acid, even at 150°, without yielding any of these compounds.

Action of Propionic Acid on Ethylic Phenanthroxylene-acetoacetate.

The action of propionic acid closely resembles that of acetic acid, except that no compound corresponding with $C_{44}H_{34}O_9$ was isolated—possibly because the reaction was conducted on too small a scale.

Ethylic phenanthroxylene-acetoacetate was heated with propionic acid in a sealed tube for one hour at 140°. There was no pressure on opening the tube, which contained a crystalline compound and a pink liquid. The crystalline compound was separated by filtration; it consisted of slender, silky needles, insoluble in the ordinary organic solvents of low boiling point, and was identical with the compound $C_{20}H_{11}O_3$, already referred to, obtained by the action of glacial acetic acid on ethylic phenanthroxylene-acetoacetate.

The pink-coloured mother liquor was poured into water, and the precipitated substance was dried and dissolved in light petroleum (b. p. 90—120°). After standing for some days, the petroleum solution deposited tufts of red crystals; these were then twice recrystallised from alcohol, after which they melted constantly at 134°. The crystals were well shaped, but still retained their red colour, which was, of course, due to the impurity already mentioned. Analysis (*v. infra*) gave figures agreeing with the formula $C_{23}H_{20}O_5$.

We then prepared the same compound by heating ethylic isophenanthroxylene-acetoacetate with propionic anhydride for three hours at 150°. It resembled in every respect the foregoing. The compound has, therefore, the formula $C_{20}H_{15}(C_3H_5O)O_4$.

	Substance.	CO_2.	H_2O.
I.	0·1915	0·5164	0·0924
II.	0·2159	0·5808	0·1024

	Calculated for $C_{20}H_{15}(C_3H_5O)O_4$.		Found. I.	Found. II.
C_{23} ……	276	73·40	73·54	73·36
H_{20} ……	20	5·32	5·36	5·27
O_5 …….	80	21·28	—	—
	376	100·00		

Analysis I was made with substance prepared from propionic acid and ethylic phenanthroxylene-acetoacetate; II, with substance from the iso-compound and propionic anhydride.

Action of Sulphuric Acid and Alcohol on Ethylic Phenanthroxylene-acetoacetate.

The results obtained in this reaction differ greatly, according to the relative proportions of alcohol and sulphuric acid employed.

Action of Alcohol containing a few drops of Sulphuric Acid.—Ethylic phenanthroxylene-acetoacetate was dissolved in a slight excess of hot absolute alcohol, a small quantity of concentrated sulphuric acid (3 drops for every 5 grams of the condensation product) was added, and the whole was heated on the water-bath for three hours. After standing over night, the solution was filtered from a little impure substance which had separated, after which it was precipitated with water. The precipitated substance was twice recrystallised from alcohol, and was thus obtained in pinkish, tabular, rectangular crystals, melting constantly at 143—144°. The pink colouring matter was partially removed by recrystallisation from light petroleum.

Analysis agreed with the formula $C_{22}H_{20}O_4$:—

	Substance.	CO_2.	H_2O.
I……	0·1803	0·5012	0·0941
II …..	0·1894	0 5279	0·0997

	Calculated for $C_{22}H_{20}O_4$.		Found. I.	Found. II.
C_{22}……..	264	75·86	75·81	76·01
H_{20} …….	20	5·75	5·79	5·84
O_4 ……..	64	18·39	—	—
	348	100·00		

Different preparations were analysed.

The compound is formed according to the equation—

$$C_{20}H_{16}O_4 + C_2H_5{\cdot}OH = C_{22}H_{20}O_4 + H_2O.$$

The formula $C_{22}H_{20}O_4$ may be expanded into

$$C_{17}H_{10}O(OC_2H_5)(COOC_2H_5).$$

The behaviour of this compound towards phenylhydrazine and caustic alkalis shows that it is closely related to the hydriodic acid reduction compound, $C_{20}H_{16}O_3$ (m. p. 124°), the formula of which may be written $C_{17}H_{11}O(COOC_2H_5)$. The compound $C_{22}H_{20}O_4$ is thus the ethoxy-derivative of the reduction compound. Both these compounds form hydrazones, showing that they contain a carbonyl group; and both are hydrolysed by caustic alkalis with simultaneous assumption of the elements of water, yielding dibasic acids; the carbonyl group being converted in this process into a carboxyl group:—

$$\underset{\substack{\text{Reduction compound}\\ \text{(m. p. 124°).}}}{C_{17}H_{11}O(COOC_2H_5)} + 2H_2O = \underset{\substack{\text{Dibasic acid}\\ \text{(m. p. 295°).}}}{C_{16}H_{12}(COOH)_2} + C_2H_5{\cdot}OH.$$

$$\underset{\substack{\text{Ethoxy-compound}\\ \text{(m. p. 141°).}}}{C_{17}H_{10}O(OC_2H_5)(COOC_2H_5)} + 2H_2O = \underset{\substack{\text{Dibasic ethoxy-acid}\\ \text{(m. p. 203°).}}}{C_{16}H_{11}(OC_2H_5)(COOH)_2}.$$

This conversion of the carbonyl into the carboxyl group must be accompanied by the opening up of the closed chain containing the carbonyl group.

Ethylic isophenanthroxylene-acetoacetate may be formulated $C_{17}H_{10}O(OH)(COOC_2H_5)$, and it might, therefore, appear that the foregoing ethoxy-compound was derived from it by the substitution of ethyl for the hydrogen of the alcoholic hydroxyl group. We do not consider, however, that this view is tenable. The iso-compound, when treated with alkali, is merely hydrolysed, yielding a *mono*basic acid; whereas if it had a constitution analogous to that of the ethoxy-compound or of the reduction compound, it ought to yield a *di*basic acid, since a hydroxyl group attached to a closed chain would probably render that closed chain more susceptible to the attack of alkalis than would an ethoxy-group, and certainly more than a hydrogen atom. It seems, therefore, necessary to assume that the closed chain contained in the iso-compound and its derivatives has a different constitution from that contained in the ethoxy-compound and in the reduction compound; and as the reduction can be obtained from the iso-compound, we must further assume that this change in constitution occurs during the reduction. Further experiment will be necessary to enable us to decide wherein this difference of constitution consists.

A further argument against the view that the ethoxy-compound is a direct derivative of the iso-compound is to be found in the fact that the latter compound is not etherified when treated in the foregoing manner with alcohol and sulphuric acid.

Action of Phenylhydrazine on the Ethoxy-compound.—When the ethoxy-compound is heated with phenylhydrazine in alcoholic solution at 100°, it forms a yellow hydrazone, very similar to that obtained from the iso-compound, and, like the latter, giving a blue coloration with concentrated sulphuric acid, but distinguished from it by its insolubility in benzene. It melts very indistinctly, with decomposition, at about 220°. A nitrogen determination agreed with the formula $C_{17}H_{10}(N_2H\cdot C_6H_5)(OC_3H_5)(COOC_2H_5)$.

0·1609 gram gave 13·50 c.c. dry nitrogen at 16° and under 482 mm. pressure. Nitric oxide absent.

	Calculated for $C_{25}H_{26}N_2O_3$.	Found.
N in 100 parts	6·39	6·31

Action of Caustic Potash on the Ethoxy-compound.—The ethoxy-compound, when boiled with aqueous caustic potash, yielded a pale yellow solution, from which hydrochloric acid precipitated the organic acid as a reddish oil, which solidified on cooling. The substance was purified by dissolving it in ethylic acetate, adding light petroleum to the hot solution until a slight turbidity was produced, and filtering from the first impure portion which separated. The filtrate deposited tufts of crystals. These were again treated in the same way, and were thus obtained colourless. They melted, with decomposition, at 203°. Benzene may also be employed as a solvent; the hot solution, on cooling, deposits nearly the whole of the substance in minute, colourless needles. Analysis gave figures agreeing with the formula $C_{16}H_{11}(OC_2H_5)(COOH)_2$:—

	Substance.	CO_2.	H_2O.
I........	0·2009	0·5250	0·0984
II........	0·2429	0·6339	0·1198

	Calculated for $C_{20}H_{18}O_5$.		Found.	
			I.	II.
C_{20}.......	240	71·01	71·27	71·17
H_{18}	18	5·32	5·44	5·48
O_5	80	23·67	—	—
	338	100·00		

The mode of formation of this acid has already been discussed.

The acid readily dissolves in aqueous ammonia, and the neutral solution of the ammonia salt gives white precipitates with silver nitrate and lead acetate and a bluish-green precipitate with copper sulphate. The silver salt was prepared for analysis. It was washed with hot and then with cold water, and dried in a vacuum. In spite of this it contained, according to analysis, a molecule of water of crystallisation; but this water was not determined directly:—

	Substance.	CO_2.	H_2O.	Ag.
I.	0·2722	0·4214	0·0798	9·1030
II.	0·2740	0·4246	0·0773	0·1035

	Calculated for $C_{20}H_{16}Ag_2O_5,H_2O$.		Found.	
			I.	II.
C_{20} ……	240	42·11	42·22	42·26
H_{18} ……	18	3·16	3·25	3·13
Ag_2 ……	216	37·89	37·84	37·77
O_6 …….	96	16·84	—	—
	570	100·00		

The methyl ester was also prepared. For this purpose, 3 grams of the acid were heated in a sealed tube with 15 grams of methyl alcohol and 10 grams of concentrated sulphuric acid for three hours at 100°. There was a strong pressure (of methyl oxide) on opening the tube. The turbid solution was precipitated with water and the precipitate recrystallised from boiling methyl alcohol. The ester was thus obtained in slender, colourless needles melting at 125°.

Analysis gave figures agreeing with the formula

$$C_{16}H_{11}(OC_2H_5)(COOCH_3)_2.$$

0·1216 gram gave 0·3215 CO_2 and 0·0655 H_2O.

	Calculated for $C_{22}H_{22}O_5$.		Found.
C_{22} ………	264	72·13	72·10
H_{22} ………	22	6·01	5·98
O_5 ……….	80	21·86	—
	366	100·00	

The ester was insoluble in carbonates. Caustic alkali hydrolysed it, and the regenerated dibasic acid melted at 202°.

Along with the foregoing ester there was formed a crystalline substance, insoluble in methyl alcohol, melting, with evolution of gas, at 243°; but the quantity was too small for further examination.

Action of Alcohol, with a Large Proportion of Sulphuric Acid, on Ethylic Phenanthroxylene-acetoacetate.—Five grams of ethylic phenanthroxylene-acetoacetate were heated with a mixture of 12 grams of concentrated sulphuric acid and 15 grams of absolute alcohol, in a sealed tube, at 100°, for one hour. A solid substance had separated, and there was considerable pressure in the tube. The contents of the tube were poured into water, and the precipitate thus obtained was filtered off and boiled with alcohol, which separated it into a soluble and an insoluble portion. The soluble portion, after purification, proved to be identical with the compound $C_{22}H_{20}O_4$ (m. p. 144°), already described, obtained by boiling the condensation product with alcohol containing a few drops of sulphuric acid. The portion insoluble in alcohol was dissolved in boiling phenol and reprecipitated by pouring the solutions into boiling alcohol, when it separated at once in yellow, glistening, microscopic, six-sided plates. It melted with decomposition, but without blackening, at 276—277°. The yield was very small, only 0·17 gram being obtained from 5 grams of the condensation product. Analysis led to the formula $C_{17}H_{12}O_2$.

0·1523 gram gave 0·4596 CO_2 and 0·0666 H_2O.

	Calculated for $C_{17}H_{12}O_2$.		Found.
C_{17}	204	82·26	82·30
H_{12}	12	4·84	4·86
O_2	32	12·90	—
	248	100·00	

The compound is formed according to the equation

$$C_{20}H_{16}O_4 + H_2O = C_{17}H_{12}O_2 + C_2H_5{\cdot}OH + CO_2,$$

and, therefore, the alcohol used in its preparation merely acts as a solvent and diluent.

Action of Alcoholic Hydrogen Chloride on Ethylic Phenanthroxylene-acetoacetate.

20 grams of ethylic phenanthroxylene-acetoacetate were dissolved in boiling absolute alcohol, and twice the volume of saturated alcoholic hydrogen chloride was added to the hot solution. After standing over night, 12 grams of a compound containing chlorine had separated. It proved to be somewhat difficult to purify, but by repeated recrystallisation, both from alcohol and from a mixture of benzene and light petroleum, it was obtained in flat, lustrous needles melting at 145—146°. A faint, brownish tinge could not be removed. The substance is readily soluble in hot alcohol and hot benzene, less soluble in hot light petroleum.

Analysis gave figures agreeing with the formula $C_{20}H_{15}ClO_3$. In the combustions a silver spiral was employed to absorb the chlorine.

	Substance.	CO_2.	H_2O.
I........	0·1992	0·5198	0·0811
II........	0·1928	0·5026	0·0809

III. 0·4045 gram gave 0·1667 gram AgCl (Carius).

	Calculated for $C_{20}H_{15}ClO_3$.		Found.		
			I.	II.	III.
C_{20}........	240·0	70·90	71·16	71·19	—
H_{15}........	15·0	4·43	4·52	4·66	—
Cl........	35·5	10·49	—	—	10·19
O_3........	48·0	14·18	—	—	—
	338·5	100·00			

The compound has been formed according to the equation

$$C_{20}H_{16}O_4 + HCl = C_{20}H_{15}ClO_3 + H_2O.$$

Action of Ammonia on the Compound $C_{20}H_{15}ClO_3$.—When the compound $C_{20}H_{15}ClO_3$ is dissolved in hot alcohol, and an excess of alcoholic ammonia is added, the solution assumes a deep-red colour, and, on standing, deposits small, yellowish crystals, whilst the colour of the liquid becomes gradually fainter, and at last disappears almost entirely. It is advantageous to work with a dilute solution, as in this way the substance is deposited at once in an almost pure condition; and this is of importance, as it cannot easily be purified by recrystallisation. It dissolves readily in acetic acid, but does not separate again from the solution. Alcohol dissolves it on prolonged boiling, but does not deposit it in a crystalline form. Ethyl acetate dissolves it only slightly, and deposits it in minute crystals. It melts, with decomposition, at 267°. It does not contain chlorine.

For analysis, the substance was not recrystallised, but merely boiled out with ethyl acetate, and dried at 100°. It gave figures agreeing with the formula $C_{40}H_{31}NO_6$.

	Substance.	CO_2.	H_2O.
I........	0·2217	0·6260	0·1039
II........	0·2336	0·6613	0·1100

Substance.		*v.*	*t.*	*p.*
III. 0·1173	dry N + NO	9·02 c.c.	19°	206 mm.
	„ N......	9·02 „	19	203 „
IV. 0·1548	dry N + NO	9·02 „	19	259 „
	„ N......	9·02 „	19	253 „

	Calculated for $C_{40}H_{31}NO_6$.		Found.			
			I.	II.	III.	IV.
C_{40}	480	77·30	77·00	77·20	—	—
H_{31}	31	4·99	5·20	5·23	—	—
N	14	2·25	—	—	2·42	2·30
O_6	96	15·46	—	—	—	—
	621	100·00				

The formula $C_{40}H_{31}NO_6$ may possibly be resolvable into $(C_{20}H_{15}O_3)_2NH$. The compound is formed according to the equation

$$2C_{20}H_{15}ClO_3 + NH_3 = (C_{20}H_{15}O_3)_2NH + 2HCl.$$

Action of Alcoholic Potash on Ethylic Phenanthroxylene-acetoacetate.

Ethylic phenanthroxylene-acetoacetate was dissolved in hot methyl alcohol, the solution was cooled quickly, and before anything had time to separate, a cold solution of caustic potash in methyl alcohol was added, and the mixture was allowed to stand in a corked flask for two days. A small quantity of a dark-brown powder, which had separated, was filtered off, but nothing was obtained from this. The filtrate was poured into excess of water, which caused a slight separation of an amorphous substance, and the diluted liquid was allowed to stand in a shallow basin for two days, in order to get rid of the methyl alcohol. This occasioned a further separation of amorphous substance, which was removed by filtration. On acidifying the filtrate with hydrochloric acid, a flocculent, yellow precipitate of an organic acid was obtained. When freshly precipitated, this acid redissolves in alkaline carbonates, but becomes insoluble by keeping. The acid, separated by filtration, and pressed to free it from excess of moisture, was at once dissolved in alcohol in the cold. Heating with alcohol prevents it from dissolving; and if the solution, prepared in the cold, is heated, insoluble matter separates. A portion of the alcoholic solution was allowed to stand, but this yielded chiefly oily products, and all attempts to purify this unstable acid failed. Another portion of the alcoholic solution was heated in a sealed tube at 100°, when almost immediately a separation of minute, glistening, yellow crystals was observed. As the quantity of this substance did not appear to increase after half an hour's heating, the tube was allowed to cool, which occasioned the separation of an oily substance. No pressure was observed on opening the tube. The substance was collected on a filter and washed with boiling alcohol, which removed the oily matter. The crystalline substance was insoluble in the ordinary organic solvents of low boiling point. It was purified by dissolving it in hot phenol and pouring the solution into boiling alcohol, when it separated immediately as a yellow, crystalline powder, which, under the microscope, was seen to consist of minute needles, generally grouped in stars or crosses; no six-sided plates could be observed. It melted, with decomposition, at 259°. The yield was very small.

Analysis gave figures agreeing with the formula $C_{17}H_{12}O_2$.

0·1000 gram gave 0·3024 CO_2 and 0·0423 H_2O.

	Calculated for $C_{17}H_{12}O_2$.		Found.
C_{17}........	204	82·26	82·47
H_{12}........	12	4·84	4·70
O_2........	32	12·90	—
	248	100·00	

This would make it isomeric with the compound obtained by heating ethylic phenanthroxylene-acetoacetate with a mixture of alcohol and concentrated sulphuric acid. As this latter compound, however, only differs from it in its somewhat higher melting point (277°), and in being precipitated from its solution in phenol in the shape of minute, six-sided plates, instead of in needles, we would not lay too much stress on this supposed isomerism, especially as we were dealing with such small quantities of substance. The two compounds may be identical.

Action of Ammonia on Ethylic Phenanthroxylene-acetoacetate.

Ethylic phenanthroxylene-acetoacetate was heated with excess of alcoholic ammonia in a sealed tube at 100° for an hour and a half. On allowing the solution thus obtained to stand, a substance crystallising in groups of lustrous, yellow laminæ was deposited. By recrystallisation from benzene it was obtained in small tufts melting, with decomposition, at 168°.

Analysis does not decide between the two formulæ $C_{40}H_{38}N_4O_5$ and $C_{40}H_{40}N_4O_4$.

Substance.		CO_2.	H_2O.
I........	0·2069	0·5514	0·1140
II........	0·2175	0·5792	0·1177

Substance		*v.*	*t.*	*p.*
III. 0·1282	dry N + NO	13·50 c.c.	16·5°	503 mm.
	,, N......	13·50 ,,	16·5	484 ,,
IV. 0·1453	dry N + NO	13·50 ,,	15·2	592 ,,
	,, N......	13·50 ,,	15·2	572 ,,

	Calc. for $C_{40}H_{38}N_4O_5$.	Calc. for $C_{40}H_{40}N_4O_5$.	Found. I.	II.	III.	IV.
C......	73·40	73·17	72·68	72·62	—	—
H......	5·81	6·09	6·12	6·01	—	—
N......	8·56	8·53	—	—	8·09	8·46
O......	12·23	12·21	—	—	—	—
	100·00	100·00				

A compound of the formula $C_{40}H_{38}N_4O_5$ would be formed according to the equation

$$2C_{20}H_{16}O_4 + 4NH_3 = C_{40}H_{38}N_4O_5 + 3H_2O,$$

whilst the formation of a compound $C_{40}H_{40}N_4O_5$ would involve a simultaneous process of reduction.

As already mentioned, we must reserve a fuller discussion of the constitution of the various compounds described in this paper until more experimental material has been collected.

We have also obtained a condensation compound from benzil and ethylic acetoacetate. It belongs to a different class from the phenanthraquinone compound, and will be described later.

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II.—*Contributions to the Knowledge of Mucic Acid.* Part IV. *Action of Phosphorus Pentachloride on Mucic Acid.*

By S. Ruhemann, Ph.D., M.A., and S. F. Dufton, B.A., B.Sc.

The investigation described in this paper was suggested by the experiments which one of us carried out in conjunction with W. J. Elliott, with the object of isolating the substances formed along with dichloromuconic acid, when mucic acid is treated with phosphorus pentachloride in the manner described by Bode. The result of the inquiry was the discovery of an acid isomeric with that found by this chemist and called by us β-dichloromuconic acid (Trans., 1890, 931).

Guided by the view that the chlorides of these two acids cannot be formed directly by the action of phosphorus pentachloride on mucic acid, but result from the splitting off of hydrogen chloride from tetrachloradipyl chloride, which may be formed as an intermediate product, we studied the action at a lower temperature than that recommended by Bode.

Though under these circumstances we found that tetrachloradipyl chloride is not formed, yet a few experiments led to observations which seemed interesting enough to pursue.

Phosphodichloromuconic Acid.

Phosphorus pentachloride has hardly any action on dry mucic acid at the ordinary temperature, but on adding phosphorus oxychloride to a mixture of 6 mols. of the chloride with 1 mol. of the acid, a slight evolution of heat takes place, and hydrogen chloride is given off. The reaction, when allowed to continue without warming, comes to an end after about 24 hours The flask now contains a white, crystalline substance suspended in the oxychloride, and also some unaltered phosphorus pentachloride which collects on the bottom of the vessel. On pouring off the oxychloride and the crystalline product suspended in it from the pentachloride, and gradually adding the mixture to powdered ice, the crystals are left undissolved. The latter are, however, slowly dissolved by cold water, more rapidly when heated, with the exception of a small quantity of a white powder which is no doubt unchanged mucic acid; the aqueous filtrate does not deposit any α-dichloromuconic acid, so that, under the conditions described above, no dichloromuconyl chloride is formed. On carefully concentrating the solution on the water-bath, or in a vacuum over sulphuric acid, large, colourless, rhombic crystals separate out, which are very soluble in water and alcohol, the solution having a strongly acid reaction.

For analysis the recrystallised substance was dried in air, and gave numbers corresponding with the formula $C_6H_4Cl_2O_4,2H_3PO_4+4H_2O$.

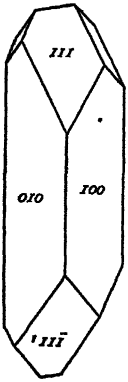
	Theory.	Found.			
		I.	II.	III.	IV.
C........	15·03	15 24	15·26	—	—
H........	3·76	3·33	3·80	—	—
Cl	14·82	—	—	15·02	—
P........	12·94	—	—	—	12·75

On drying over sulphuric acid in a vacuum, this compound lost in weight 11·31 per cent., corresponding to 3 mols. H_2O, which require 11·27 per cent. On drying at 100°, a further loss of 3·74 per cent. took place, corresponding to 1 mol. H_2O, which requires 3·76 per cent.

The anhydrous acid melts with decomposition at about 185°.

Mr. R. H. Solly has been kind enough to provide us with the following crystallographic data of this acid.

FIG. 1.



System: Orthorhombic—

$$a : b : c = 0{\cdot}62812 : 1 : 0{\cdot}29274.$$

100 : 110 = 0·32° 18′; 010 : 011 = 73° 41′; 001 : 101 = 24° 57′.

Forms observed—

*a*100, *b*010, *p*111, *n*101, *e*011.

	Observed.	Calculated.	No. of edges.	Limits.
ap......	66° 3′	66° 3′	7	66—66° 9′
bp......	74 13	74 13	7	74° 1′—74° 20′
pp_{II}	58 36	58 30	5	58 8—59 2

No measurements were obtained from *n* and *e*. The crystals are limpid, the faces are always pitted, the *a* and *b* faces have good lustre, but the *p* planes are usually rounded and give poor reflections.

The *a* and *b* faces are often evenly developed, but the *p* ones are peculiarly unequally developed, resembling crystals of the mineral meionite at one end of the *c* axis; but have the planes parallel to the *c* plane evenly developed as shown in the figure. The faces *n* and *e* are very narrow and truncate the edges of pp_I and p_I and $p_I p_{II}$.

Cleavage *a* fairly perfect.

Optical characters AE = *b*.

1st mean line *a*.

Sign of double refraction *positive*.

The optic angle in air for Na 75° 25′; $\rho < \nu$, weak.

The formula given above represents this acid as a compound of dichloromuconic acid with phosphoric acid; it may, therefore, be called phosphodichloromuconic acid. The phosphoric acid is chemically combined in the molecule, and cannot be detected by magnesia mixture, but the acid gives a yellow precipitate with ammonium molybdate when previously heated with nitric acid.

The new acid contains in its molecule dichloromuconic acid, for on warming it with concentrated sulphuric acid, or by heating the aqueous solution in a sealed tube at 100° for several hours, α-dichloromuconic acid is produced. On account of the new substance undergoing decomposition in this way, it is necessary, in its preparation, to concentrate the aqueous solution at a low temperature, otherwise part of it undergoes the same change.

If we accept for dichloromuconic acid the generally adopted, though not yet proved, expression

$$\mathrm{COOH{\cdot}CH{:}CCl{\cdot}CCl{:}CH{\cdot}COOH},$$

the phospho-acid may be represented by the formula

$$\mathrm{COOH{\cdot}CH(OH){\cdot}CCl(H_2PO_3){\cdot}CCl(H_2PO_3){\cdot}CH(OH){\cdot}COOH}.$$

That the two molecules of phosphoric acid are distributed in this manner is supported by the following experiments.

The phosphodichloromuconic acid has, as stated before, a strongly acid reaction. A solution of 0·0864 gram of the acid required for neutralisation a volume of titrated potash containing 0·0403 gram KOH, which corresponds to 46·64 per cent. KOH. This shows that 4 mols. of KHO (46·76 per cent.) are required to neutralise 1 mol. of the acid. If, however, potash is added to an excess of the acid dissolved in water, colourless crystals of a salt containing two atoms of potassium separate out.

The formula $C_6H_8K_2Cl_2P_2O_{12}$ requires :—

	Theory.	Found. I.	Found. II.
K	16·15	16·6	16·37

This potassium salt has, as might be expected, acid properties; it is sparingly soluble in cold, more readily in boiling water.

Barium Salt.—If barium chloride is added to a solution of the phospho-acid, a barium salt is precipitated after some time in colourless crystals which, once formed, are only slightly soluble in water. This salt contains two atoms of barium and has, when dried at 100°, the composition $C_6H_6Ba_2Cl_2P_2O_{12} + H_2O$, as indicated by the following analyses :—

	Theory.	Found. I.	II.	III.
Ba........	39·42	39·40	39·20	39·43

The salt does not lose its water of crystallisation at 140°, and decomposes at a higher temperature.

Aniline Salt.—In an alcoholic solution of the acid, aniline produces a white precipitate which, washed with alcohol and dried at 100°, has the formula $C_6H_4Cl_2O_4,2H_3PO_4,2C_6H_5{\cdot}NH_2$.

	Theory.	Found. I.	II.
N	4·72	4·95	—
Cl	11·97	—	12·22

This salt crystallises from water in colourless prisms, and its solution is acid to litmus paper.

The composition of these salts shows that two or four hydrogen atoms in phosphodichloromuconic acid are capable of undergoing substitution. According to the formula for the acid given above, it should have six replaceable hydrogen atoms, and indeed in the ammonium salt, we have a compound containing 6 mols. of NH_4.

Ammonium Salt.—This is formed by adding an excess of aqueous ammonia to the solution of the acid in water, when, if the solutions are concentrated, the salt is thrown down at once in the form of colourless, oblique crystals. These lose their lustre on drying over sulphuric acid, and give off ammonia when heated alone or with water.

For analysis, they were dried in air, and gave numbers corresponding with the formula $C_6H_4Cl_2O_4,2H_3PO_4,6NH_3 + 5H_2O$:—

	Theory.	Found. I.	II.	III.
N	14·02	14·32	—	—
P..........	10·35	—	10·28	—
Cl	12·02	—	—	11·87

The properties and the composition of the salts of phosphodichloromuconic acid, and especially those of the ammonium salt, support the view expressed above of the constitution of the acid; it is to be regarded as hexabasic, and may be formulated—

$$COOH{\cdot}CH(OH){\cdot}CCl(H_2PO_3){\cdot}CCl(H_2PO_3){\cdot}CH(OH){\cdot}COOH,$$

if the formula for dichloromuconic acid,

$$COOH{\cdot}CH{:}CCl{\cdot}CCl{:}CH{\cdot}COOH,$$

be correct. This view is confirmed by the study of the product, which, under the influence of water, is transformed into the phospho-acid.

Phosphodichloromuconyl Chloride.

The action of phosphorus pentachloride and oxychloride on mucic acid at the ordinary temperature gives rise to a product which still contains a small quantity of unchanged mucic acid.

The observation that the crystalline substance, thus formed, is soluble in warm phosphorus oxychloride gave the key to a method for its purification. If the mixture obtained in the reaction be heated to 100°, and quickly filtered through glass wool, the clear liquid, on cooling, deposits colourless plates which, collected, washed with dry benzene, and dried over sulphuric acid, gave numbers corresponding with the formula

$$COCl{\cdot}CH(OH){\cdot}CCl(POCl_2){\cdot}CCl(POCl_2){\cdot}CH(OH){\cdot}COCl.$$

		Found.		
	Theory.	I.	II.	III.
C	13·90	14·15	—	—
H	0·77	0·85	—	—
Cl........	54·82	—	54·56	—
P	11·97	—	—	12·17

This substance is identical with the crystals formed in the cold. It dissolves in water without leaving any residue, and the solution on concentration deposits the characteristic rhombic crystals of phosphodichloromuconic acid.

The fact that the former compound is stable at 100° allows of its preparation without using phosphorus oxychloride. Bode had already observed that the action of phosphorus pentachloride on mucic acid starts at 70° and is completed at 100°. If the almost clear liquid, thus obtained, be quickly filtered, the above mentioned compound will crystallise out on cooling.

The formation of this substance and the transformation it undergoes when treated with water show that the action of phosphorus pentachloride on mucic acid differs with the temperature: at 100°, the phospho-acid chloride is produced; at 120°, dichloromuconyl chloride. It was, therefore, to be expected that the product formed at a lower temperature would, when heated with phosphorus pentachloride at 120°, yield dichloromuconyl chloride. This is indeed the case; a mixture of 1 mol. of the former and 2 mols. of phosphorus pentachloride, when digested at 120°, evolves hydrogen chloride; the mass becomes liquid, and on cooling deposits dichloromuconyl chloride ; the reaction may be expressed by the equation :—

$$\begin{aligned}&\mathrm{COCl{\cdot}CH(OH){\cdot}CCl(POCl_2){\cdot}CCl(POCl_2){\cdot}CH(OH){\cdot}COCl + 2PCl_5}\\ &\qquad = \mathrm{COCl{\cdot}CH{:}CCl{\cdot}CCl{:}CH{\cdot}COCl + 4POCl_3 + 2HCl.}\end{aligned}$$

This chloride, on the addition of water, is transformed into the characteristic needles of α-dichloromuconic acid. The latter may also be obtained from the phosphodichloromuconyl chloride by warming with concentrated sulphuric acid, when it dissolves, and, on pouring into water, Bode's acid is precipitated.

Whilst the phosphodichloromuconyl chloride yields, by the action of water, the phospho-acid, it suffers a different transformation under the influence of alkali or ammonia, and these changes throw light upon the relationship between Bode's dichloromuconic acid and the β-acid.

On adding phosphodichloromuconyl chloride to potash, it dissolves with evolution of heat, and addition of hydrochloric acid to the cold solution precipitates α-dichloromuconic acid. The filtrate from this acid, when extracted with ether, yields the β-acid.

Aqueous ammonia acts violently upon the phospho-acid chloride forming the amides of α- and β-dichloromuconic acids, which are precipitated as a white powder in the course of the reaction. Their separation was effected by extracting with boiling water; the hot filtrate, on cooling, deposits colourless needles, which by their properties and a nitrogen determination were recognised as β-dichloromuconamide.

The formula $C_6H_6Cl_2N_2O_2$ requires :—

	Theory.	Found.
N	13·40	13·66

The residue left undissolved by water is sparingly soluble in alcohol, and is the amide of α-dichloromuconic acid, as indicated by the following nitrogen determination, which gave :—

	Theory for $C_6H_6Cl_2N_2O_2$.	Found.
N	13·40	13·70

If, on the one hand, the observations described above explain satisfactorily the action of phosphorus pentachloride on mucic acid, on the other hand, they throw light upon the relationship between α- and β-dichloromuconic acids. Both acids are produced from the phospho-acid chloride, which, on treatment with water, yields only one phospho-acid, as indicated by the crystallographic measurements; they are, therefore, most probably stereochemical isomerides.

This view is confirmed by the ready transformation of the β-acid into Bode's dichloromuconic acid. On adding a small quantity of bromine-water to a cold aqueous solution of the former, and allowing the mixture to stand for some time, the whole sets to a mass of crystals which do not contain bromine, but are simply α-dichloromuconic acid, as indicated by its properties and by the following analysis :—

The formula $C_6H_4Cl_2O_2$ requires :—

	Theory.	Found.	
		I.	II.
C	34·12	34·09	—
H	1·90	2·00	—
Cl	33·65	—	33·62

The isomeric dichloromuconic acids may be regarded, therefore, as bearing the same relation to one another as fumaric to maleïc acid, the latter being completely changed into fumaric acid, by the action of haloid acids (Kekulé, *Annalen*, Suppl. 1, 134), and, partially, by bromine (Petri, *Annalen*, **195**, 59).

If Wislicenus' view with regard to the transformation of maleïc acid into fumaric acid be accepted, that one molecule of the halogen or haloid acid is first added, that then rotation of the system takes place, and that finally the halogen or haloid acid splits off again, leaving the isomeric acid, then we may assume the change of β-dichloromuconic acid into the α-acid to be brought about by bromine in the same manner.

University Laboratory,
Cambridge.

III.—*Note on Normal and Iso-propylparatoluidine.*

By E. Hori and H. F. Morley.

In connection with an investigation which we undertook three or four years ago, we thought it desirable to be able to distinguish with certainty between normal and iso-propylparatoluidine. We had completed the examination of this point when the investigation of which this was to form a part was brought to an abrupt termination by the departure of one of us from England. Nevertheless, we think that the following observations, made in 1887, ought, perhaps, to be recorded.

Isopropylparatoluidine.

An almost theoretical yield of isopropyltoluidine may be obtained by heating isopropyl iodide with paratoluidine in equimolecular proportions for two days in sealed tubes at 130°. The isopropyl iodide employed was obtained in the usual way from glycerol, iodine, and amorphous phosphorus, and boiled at 89—91°. The crude isopropylparatoluidine was purified by conversion into its nitrosamine, the nitrosamine being then reconverted into the base by treatment with tin and hydrogen chloride.

Isopropylparatolylnitrosamine, $(CH_3)_2CH{\cdot}N(NO){\cdot}C_6H_4{\cdot}CH_3$, separates from alcohol in beautiful, slightly yellowish crystals, melting at 58—59° (uncorr.). It is easily soluble in ether, benzene, alcohol, and glacial acetic acid, but insoluble in water. It cannot be distilled with steam.

100 grams of alcohol (98½ per cent.) dissolve 65 grams of the nitrosamine at 22°. On combustion, 0 2598 gram of the substance gave 35 c.c. of nitrogen at 18° C. and 754 mm. bar. pressure corresponding to 15·89 per cent. nitrogen, the calculated percentage being 15·73.

In the conversion of the nitrosamine into isopropylparatoluidine by warming with tin and hydrogen chloride solution, a yield of only 60 per cent. of the theoretical amount was obtained, but we failed to improve this yield by other methods of effecting the conversion.

Isopropylparatoluidine may also be prepared from diazotoluenetoluide, $C_7H_7{\cdot}N_2{\cdot}NH{\cdot}C_7H_7$, an alcoholic solution of sodium ethylate, and isopropyl iodide by heating the mixture for five hours on the water-bath, distilling off the alcohol, pouring the solution into cold water, and decomposing the precipitate with hydrogen chloride; but the yield in this case is not very good.

Isopropylparatoluidine is a colourless oil, which slowly becomes coloured. It boils at 219° to 221° (uncorr.). Its *density* is 0·9226 gram per c.c. at 20°, 0·9209 at 23°, 0·9129 at 35°, 0 8988 at 51°, and 0·8937 at 56°. The density at its boiling point, determined by Ramsay's method, was found in three experiments to be 0·7469, 0·7452, and 0·7477, the mean being 0·7466. This gives a molecular specific volume of 199·57, whilst Brühl's formula for specific volumes would give 199·50 as the calculated number.

The index of refraction was kindly determined by Dr. A. H. Fison, of University College, to be as follows:—

Line.	Wave-length.	Index of refraction.
H_α	·6562	1·5277
D	5892	1·5322
H_β	4861	1·5473

Calculating the molecular refractive energy from the values for the lines H_α and H_β, we obtain 81·4 instead of the theoretical number 79·3.

Normal Isopropylparatoluidine Oxalate, $(C_{10}H_{15}N)_2,H_2C_2O_4$.—The base forms both a normal and an acid oxalate, but the latter being exceedingly soluble both in water and alcohol is not easily crystallised, whilst the former is only slightly soluble in cold water, and can be easily crystallised from alcohol.

The normal oxalate crystallises from hot absolute alcohol in colourless crystals melting at 129—130° (uncorr.). Three determinations of oxalic acid gave 23·02, 23·26, and 23·18 per cent. respectively (calculated 23·19). The salt is almost insoluble in cold water, but on warming it dissolves with partial separation of the base. 100 grams of alcohol (98½ per cent.) dissolve 4·76 grams at 17° and 5·76 grams at 22°.

Isopropylparatoluidine Hydrochloride, $C_{10}H_{15}N,HCl$.—This salt, which separates as colourless crystals, on passing hydrogen chloride into a solution of the base in ether, crystallises from alcohol in large crystals of wax-like colour melting at 170—171°. It is very easily soluble both in water and alcohol, slightly in cold benzene, and easily in boiling benzene, from which it separates in needles [Cl = 18·69 and 18·63; calc. 19·13].

The *ferrocyanide*, $(C_{10}H_{15}N)_2,H_4FeCy_6$, obtained by precipitation, is a white powder [Fe = 11·55 and 11·12; calc. 10·89].

Normal Propylparatoluidine.

Normal propylparatoluidine was prepared by heating equimolecular weights of normal propyl iodide and paratoluidine for two days in sealed tubes at 160°; the yield being 90 per cent. of the theoretical. The normal propyl iodide used was prepared from propyl alcohol, amorphous phosphorus, and iodine, and boiled at 101—103° (uncorr.). The normal propylparatoluidine was purified, like its isomeride, by conversion into its nitrosamine.

Normal Propylparatolylnitrosamine, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}N(NO){\cdot}C_6H_4{\cdot}CH_3$, is an oil, not solidifying at −20°. On heating, it begins to decompose below 100°, giving off nitrous fumes. In converting it into normal propylparatoluidine, the yield is only 50 per cent., and the boiling point of the resulting base is not so sharp as that of its isomeride, so that some fractional distillation is necessary.

Normal Propylparatoluidine is a colourless oil, boiling at 230—233°, and does not become much coloured even on standing for a long time. Its solubility is 0·9243 gram per c.c. at 20°, 0·9296 at 23°, 0·9172 at 35°, and 0·9053 at 51°. The density at the boiling point was found in four determinations to be 0·7554, 0·7546, 0·7533, and 0·7539, the mean being 0·7543. This gives a molecular specific volume 197·53 (theory 199·50).

The index of refraction was kindly determined by Dr. Fison to be as follows:—

H_α	1·5306
D	1·5367
H_β	1·5495

The molecular refractive energy $\left(\frac{\mu_A - 1}{d}\right)M$ calculated from the values for H_α and H_β is 82·5.

Oxalates of Normal Propylparatoluidine.—Normal propylparatoluidine forms both normal and acid oxalates; but the normal oxalate, when in solution, easily decomposes into the acid oxalate and the base, and it is, therefore, difficult to obtain it in a crystalline state.

The acid oxalate, $(C_{10}H_{15}N),C_2H_2O_4$, crystallises from alcohol, and melts at 172—173° with decomposition. The percentage of oxalic acid was found to be 37·86 and 37·64 (calculated 37·65). The acid oxalate is only slightly soluble in cold water and alcohol, but easily dissolves on warming. 100 grams of alcohol (98½ per cent.) dissolve 1·4 grams at 21°.

On mixing equimolecular proportions of the base and oxalic acid, both in alcoholic solution, a precipitate of the acid oxalate is obtained, but the filtrate, when left to evaporate spontaneously, deposits white powdery crystals of the normal salt $(C_{10}H_{15}N)_2,C_2H_2O_4$ [Percentage of oxalic acid found: 23·25 and 23·08; calc. 23·19]. The normal oxalate can also be obtained by adding a large excess of the base to a cold alcoholic solution of the acid oxalate, when crystals of the normal salt often separate at once, and further quantities may be obtained by spontaneous evaporation.

The normal oxalate of normal propylparatoluidine melts at 116—117°, and is more soluble both in water and in alcohol than the acid salt.

Its aqueous solution when warmed becomes milky, from separation of the base, but becomes clear again on cooling. If the solution is heated to boiling, it deposits, on cooling, the acid oxalate only.

Normal and iso-propylparatoluidines may be separated through the difference in the solubility and stability of their oxalates. If a mixture of the two bases be gradually added to an aqueous solution of oxalic acid, sufficient to form acid oxalates, a crystalline precipitate of the acid oxalate of normal propylparatoluidine is formed. On evaporating the filtrate, and allowing it to cool, more of this salt separates, but after repeating this process several times distinct crystals of the oxalate of isopropylparatoluidine begin to appear. On adding potash to the mother liquor at this point, almost pure isopropylparatoluidine is liberated.

The *hydrochloride* of normal propylparatoluidine, $C_{10}H_{15}N,HCl$, crystallises from boiling benzene in needles melting at 150—151° [Cl = 18·95 per cent.; calc. 19·13 per cent.]. It is very soluble in water and alcohol, slightly soluble in cold benzene, easily soluble in boiling benzene.

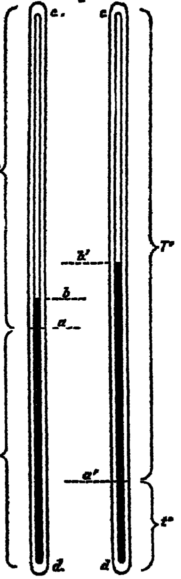
The *ferrocyanide* of normal propylparatoluidine, $(C_{10}H_{15}N)_2,H_4FeCy_6$, is a white solid, turning blue on exposure to light [Fe = 11·09 per cent.; calc. 10·89].

IV.—*A New Method of Determining the Specific Volumes of Liquids and of their Saturated Vapours.*

By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

IF a closed graduated tube, containing a known volume of liquid at a given low temperature *t*°, be heated to some higher temperature T°, the liquid will expand, but the apparent expansion will be smaller than the real, on account of the evaporation of a portion of the liquid. If the density of the saturated vapour, or the ratio of the specific volume of the vapour to that of the liquid at T° is known, the necessary correction may be applied, but at temperatures above the ordinary boiling point of the liquid this is usually not the case. Suppose now that by some suitable arrangement one portion *ca* of the tube *cd* (p. 38) can be heated to T°, the remainder of the tube, *ad*, being kept at a constant low temperature *t*°, and that by moving the tube, or the heating apparatus, a greater length *ca′* of the tube can subsequently be heated to T°, then we shall have a second method of determining the apparent expansion of the liquid. For a known volume of the liquid *aa′* at *t*° has been heated to T°, and has expanded from *b* to *b′*. But in this case the space above the liquid is always filled with saturated vapour, and since the volume *cb′* is less than *cb*, the apparent expansion is greater than the real, for the vapour originally occupying the volume *bb′* has now condensed. Here again, the ratio of the specific volume of the saturated vapour to that of the liquid at T° being usually unknown, it is impossible to calculate the true expansion from *t*° to T°. But since by each method we have the same two unknown values—the true volume of the liquid and the ratio of the specific volume of the vapour to that of the liquid—we

Fig I.



can obtain two equations from the experimental data, from which both values may be calculated.

Let V_T be the true volume of the liquid at T°, and r the ratio of the specific volume of saturated vapour to that of liquid at T°.

In the first experiment, when the whole tube is heated to T°, let V'_T be the apparent volume of the liquid, and V_c the volume of saturated vapour. Then the volume of liquid at T°, formed by the condensation of the saturated vapour V_c, would be V_c/r, and the true volume of liquid at T° =

$$V_T = V'_T + \frac{V_c}{r}.$$

In the second experiment, let V_t be the total volume of liquid at t, V_A the volume of liquid between a and a', and V_B the apparent expansion from b to b'.

Then, since V_A volumes of liquid at $t°$ expand so as to occupy the volume $V_A + V_B$ at T°, the total volume of liquid V_t would, under the same conditions, occupy the volume $\frac{V_t}{V_A}(V_A + V_B)$. But in consequence of the expansion a certain amount of the saturated vapour has condensed, and the error due to condensation—calculated for the total volume of liquid—will be $\frac{V_t}{V_A} \cdot \frac{V_B}{r}$. Therefore, the true volume of liquid at T° will be

$$V_T = \frac{V_t}{V_A}(V_A + V_L) - \frac{V_t}{V_A} \cdot \frac{V_B}{r}.$$

From these two equations we have

$$V_T = \frac{V_t\{V_c(V_A + V_R) + V_B V'_T\}}{V_B V_t + V_c V_A}.$$

and the ratio of the specific volume of saturated vapour to that of liquid at T° will be

$$r = \frac{V_c}{V_L - V'_T}.$$

Lastly, the specific volume (volume of 1 gram) of liquid at T° will be

$$S_T = \frac{V_T \times S_t}{V_t},$$

where S_t is the volume of 1 gram at $t°$; and the specific volume of the saturated vapour at T° will be

$$s_T = r \times S_T.$$

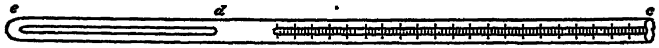
It is of course impossible to heat the whole of one portion of a tube strongly, and to keep the whole of the remainder of the tube at a low temperature; there must be an intermediate portion, one extremity of which is at the higher temperature, the other at the lower, the temperature falling gradually from one extremity to the other. If, however, in both stages of the second experiment there is a similar gradation of temperature, though of course in different parts of the tube, the results will not be affected provided that the tube is of even bore.

I have succeeded in devising an apparatus by which the specific volumes of liquids and saturated vapours may be determined by the method described, and as *the method is applicable to liquids which attack mercury, and may be employed through a wide range of temperatures*, it seems desirable to give a detailed account of it.

A piece of barometer tubing, of very even bore and of about 60 cm. length, is closed at the blowpipe at *d* (Fig. 2, p. 40), about 20 cm. from one end, the closed part being carefully rounded. The portion of the tube *de* serves as a handle, and the end *e* may conveniently be closed.

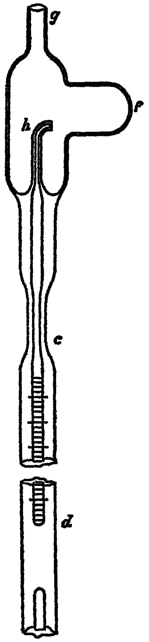
The tube from *d* to *c* is then graduated in millimetres, and calibrated in the usual manner by weighing with mercury.

Fig 2.



The end *c* is then sealed to the apparatus shown in Fig 3, and the whole apparatus is thoroughly dried by repeatedly exhausting and allowing dry air to enter.

Fig. 3.

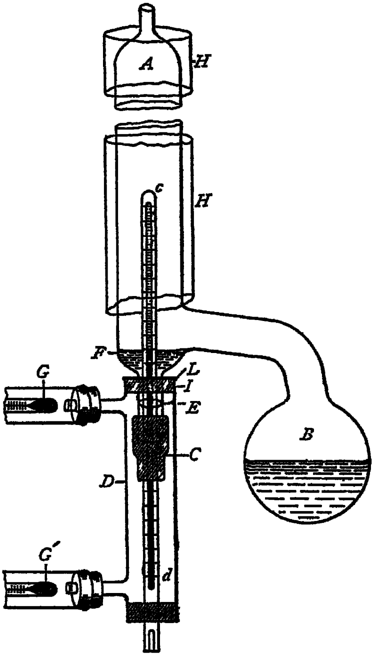


The freshly distilled liquid is then admitted into the apparatus at *g*, either by means of a fine funnel, or, if the liquid is hygroscopic, by means of a siphon arrangement such as that described by Thorpe (Trans., 1880, **37**, 22), until the wide protuberance *f* is about one-third filled. A piece of thick-walled indiarubber tubing, provided with a screw clip, is then passed over *g*, and the apparatus is connected with a pump and exhausted. The clip is then closed, the apparatus removed from the pump, and the liquid in the tube *cd* made to boil vigorously for some time, so as to completely remove air adhering to the walls of the tube. (The narrow tube *h*, drawn out and bent at the end, prevents the projection of the liquid against the indiarubber.) Lastly, the liquid is allowed to fill the tube completely, and is then boiled from above downwards until only the required amount remains in the tube, when the apparatus is tilted, so that the greater part of the liquid above *h* flows into *f*. The tube is then at once sealed at *c*, the glass being allowed to fall together, so as to withstand a high internal pressure.

The volume of liquid is then measured, either at 0° or with the tube surrounded by running water of known temperature. The total volume of the tube, which is as yet unknown, is easily ascertained by inverting the tube, so that all the liquid flows to the other end, and taking a second reading. The sum of the two readings gives the total volume, but as the tube was calibrated with mercury, which has a convex meniscus, while that of the liquid is concave, the first reading must be corrected for this reversal of meniscus. When the tube is inverted, the concave meniscus of the liquid corresponds in position with the convex meniscus of mercury during calibration, and no correction is required.

The arrangement for heating the tube is shown in Fig. 4. *AB* is a jacketing tube, containing a pure liquid which is to be boiled under

Fig. 4.



known pressures The lower end of the jacketing tube is narrow, and is provided with a piece of indiarubber tubing, *C*, through which the volume tube *cd* passes. A current of cold water passes through the tube *D*, and keeps the lower part of the volume tube at a constant temperature, which is measured by the thermometers *GG'*. If the indiarubber tube *C* has been kept under water for several hours before it is placed on the jacketing tube, the volume tube may easily be pushed up through it; but, notwithstanding the reduced pressure in the jacketing tube, no water passes up between the indiarubber and the volume tube.

A ring of lead, *L*, is placed above the indiarubber cork *I*, so that the jacketing tube *D* may always be pushed up to exactly the same height.

The position of the volume tube in the jacketing tube is shown by a horizontal line *E*, etched on the narrow part of the jacketing tube. The scale divisions on the volume tube corresponding to this etched line give the readings *a* and *a'* (Fig. 1, p. 38). The jacketing tube is protected from draughts by the outer tube *HH*, the space between *A* and *H* at the top being closed by a ring of asbestos cardboard.

The experiment is begun with the volume tube in the position shown in the diagram. The liquid in *B* is made to boil, and when the vapour has reached the top of the jacketing tube, and the pressure has been regulated to give the desired temperature, the volume tube is pushed up until the liquid in it is about 25 mm. above the level of the liquid *F*.

The reading *a* may be taken at once, but the height *b* of the liquid in the volume tube does not become constant until the liquid *F* (Fig. 4, p. 41), which has been cooled to some extent by pushing up the cold tube, has regained its original temperature. From 15 to 20 minutes are required before the reading of *b* becomes quite constant, but it is advisable to take readings every few minutes until constancy has been attained.

The volume tube is now pushed up again until the bottom of the tube *d* is about 10 or 20 mm. below *E*, when the readings *a* and *b'* are taken in the same manner as before.

Lastly, the volume tube is pushed up until *d* is about 25 mm. above *F*, when, of course, the whole of the liquid is heated, and the reading V' is taken. In this case, the reading becomes constant after three or four minutes.

The expansion of the liquid at low temperatures having been determined in the ordinary way, the volume V_t at the temperature *t* of the flowing water may be calculated or read from a curve, and we have now all the data required for calculating the specific volumes of the liquid and saturated vapour at T°.

It is necessary, however, to apply the following corrections :—

1. The apparent volume of liquid at the ordinary temperature or 0° is slightly too small, as a certain quantity of the substance is present in the form of saturated vapour. The correction, which is very small, may be made on the assumption that the density of the saturated vapour is normal.
2. The expansion of the glass must be allowed for in the calculation of V_B, V'_T, and V_c. It is generally too small to affect the value of V_A.

In order to test the accuracy of the method, as regards the determination of the specific volumes of liquids, experiments were made with benzene and carbon tetrachloride, for which substances accurate data have been obtained by the method employed in the investigations of the benzene derivatives (Trans., 1889, 55, 486). In the experiments with carbon tetrachloride, however, and in the earlier ones with benzene, the water jacket was not employed. A comparison of the two series of determinations with benzene shows that more accurate results are obtained by the addition of the water jacket:—

The results by the old and new methods are given in the following tables :—

Carbon Tetrachloride (without Water Jacket).

Temperature.	Volume of 1 gram liquid.		Difference per cent.
	Old method from curve.	New method.	
100	0·6972	0·6961	−0·16
200	0·8408	0·8418	+0·12
210	0·8637	0·8661	+0·30
220	0·8898	0·8899	+0·01
230	0·9199	0·9219	+0·24
250	0·9998	1·0029	+0·48
260	1·0590	1·0660	+0·66

Benzene (without Water Jacket).

Temperature.	Volume of 1 gram liquid.		Difference per cent.
	Old method from curve.	New method.	
100	1·2616	1·2607	−0·07
130	1·3214	1·3191	−0·17
160	1·3918	1·3877	−0·29
190	1·4797	1·4815	+0·12
220	1·5973	1·6006	+0·21
240	1·7092	1·7174	+0·48
260	1·8770	1·8845	+0·40
Benzene (with Water Jacket).			
160	1·3918	1·3931	+0·09
170	1·4186	1·4202	+0·11
240	1·7092	1·7123	+0·18
260	1·8770	1·8809	+0·21

It will be seen that in the four determinations with the water jacket the greatest error is only 0·21 per cent., and that even without the water jacket the errors do not exceed 0·3 per cent., except at the highest temperatures.

The chief value of the method depends on the fact that it can be employed for the determination of the expansion of liquids such as nitrogen peroxide, bromine, or chlorine compounds which attack mercury.

Specific Volumes of Saturated Vapour.

The ratio of the specific volume of saturated vapour to that of liquid at T° is given by the equation

$$r = \frac{V_c}{V_T - V'_T},$$

where V_c is the volume of saturated vapour in the tube, V_T the true volume of liquid, supposing all the vapour to be condensed, and V'_T the observed volume of liquid.

It is clear that accurate results can only be obtained when the value $V_T - V'_T$ is fairly large, otherwise a small error in either V_T or V'_T would mean a relatively very much larger error in their difference, and therefore in the value of r.

With a tube of the form employed, the results are sufficiently accurate only at high temperatures, at which the density of the saturated vapour is considerable. At low temperatures the volume of the saturated vapour relatively to that of the liquid should be greatly increased.

Of the three values V_c, V'_T, and V_T, the two first are obtained by direct reading, and may therefore be considered as very accurately determined. On the other hand, the calculation of V_T depends on a number of readings, and this value is therefore subject to greater chances of error.

If, therefore, better values of V_T than those afforded by the new method are available, it is better to make use of them. Now the specific volumes of liquids, as determined by the old method (*Phil. Trans.*, 178, 57), are calculated from a single reading in each case, and the values of V_T can be calculated directly from them.

In the case, therefore, of substances which do not attack mercury, the best results will be obtained by determining the specific volumes of the liquid by the old method, and the values V_c and V'_T by the new. There is also the great advantage that the time required for each determination of V'_T and V_c is very small, for as the whole of the liquid is heated, the position of the volume tube in the jacketing tube does not require to be altered during the experiments.

I have determined the values of V'_T and V_c for carbon tetrachloride in this manner at other temperatures in addition to those given in the previous tables, and though I have as yet no means of testing the accuracy of the results, it may be worth while to give all those obtained at high temperatures.

Carbon Tetrachloride.

Temperature.	V_c.	V_T.	V'_T.	r_T.	Volume of 1 gram saturated vapour.
160	0·8592	0·5633	0·5402	37·00	28·50
170	0·8534	0·5743	0·5464	30·50	24·00
180	0·8479	0·5864	0·5523	24·90	19·90
190	0·8425	0·5998	0·5581	20·20	16·60
200	0·8369	0·6149	0·5640	16·40	13·80
210	0·8313	0·6316	0·5699	13·50	11·60
220	0·8259	0·6507	0·5758	11·00	9·81
230	0·8206	0·6727	0·5814	8·99	8·27
240	0·8157	0·6987	0·5866	7·28	6·95
250	0·8116	0·7311	0·5911	5·80	5·80
260	0·8094	0·7743	0·5936	4·48	4·74
270	0·8120	0·8395	0·5914	3·27	3·76
280·45	0·8400	0·9675	0·5638	2·08	2·75

The last two values of V_T are somewhat uncertain, as carbon tetrachloride attacks mercury at high temperatures, and the values of V_T were calculated from the results by the old method.

I hope before long to be able to obtain some determinations of the volumes of a gram of the saturated vapours of the haloid derivatives of benzene, in order to find whether the generalisation of Van der Waals holds good for these substances in the state of saturated vapour as well as in the liquid state.

V.—*The Estimation of Cane-sugar.*

By C. O'Sullivan, F.R.S., and Frederic W. Tompson.

The accurate estimation of sucrose in the presence of other carbohydrates has always been attended with considerable difficulty; indeed, in many cases, it was not found possible until Kjeldahl, in 1881, published a paper on the carbohydrates of malt (*Meddelelser*, 1881, 337). Some time afterwards, in a paper by one of us on the same subject, a method of estimating cane-sugar was given almost identical with his (Trans.. 1886, 49, 58). In both cases very accurate results were obtained, and, as the latter paper was published in ignorance of Kjeldahl's work, it may be regarded as an independent confirmation of it.

It is obvious that in solutions such as those obtained from malt, the usual method of estimating cane-sugar with acid is inapplicable on account of the action of the acid on the other carbohydrates. Indeed, this is the case in nearly all solutions obtained from natural sources. This difficulty was overcome by the use of the enzyme, invertase, and it was employed either in the form of a soluble preparation, or, in the raw state, as brewers' yeast, together with sufficient thymol to prevent fermentation and growth of yeast. By this means the cane-sugar was inverted without any other substance present being altered, and the results thus obtained were perfectly trustworthy. The decrease in optical activity, and the increase in cupric reducing power, each formed a measure of the amount of sucrose originally present in the solution. Very concordant results were obtained.

The estimation of cane-sugar by means of invertase is without doubt a perfectly satisfactory process. The only disadvantage consists in the difficulty of preparing the invertase. Until the recent publication of our paper on invertase (Trans., 1890, 57, 834), this objection was practically fatal, and it still forms a great drawback to the universal application of the process, as it takes at least three weeks to prepare invertase by our method.*

The use of yeast as the hydrolyst has hitherto been held to require the presence of some such substance as thymol, to prevent fermentation, and this method has not generally been considered to be so reliable as the former one.

It is the purpose of the present paper to show that the process known commercially as "Tompson's Inversion Process" is perfectly applicable to the estimation of cane-sugar. In this process, ordinary brewers' yeast is employed as the hydrolytic agent without the addition of anything else. We shall show that we have in this method a simple and convenient means of estimating cane-sugar independently of other substances in solution, and that the results obtained are accurate and trustworthy.

Our procedure is as follows:—The solution containing the cane-sugar must be approximately neutral (certainly not alkaline), and if the presence of any enzyme is suspected, the temperature should be momentarily raised to 80° to destroy it. The optical activity at 15·5° and the cupric reducing power of the solution are determined,† and then 50 c.c. of it are poured into a beaker and raised to a temperature of 55° in a constant temperature bath. Some ordinary brewers' yeast, pressed in a towel, is now taken. The weight of the pressed yeast should be about 1/10th of the total amount of sugar to be inverted.‡ It is thrown into the hot solution, and the whole gently stirred until mixture is complete. The solution is left for 4 hours in the water-bath: at the end of this time it is cooled to 15·5°, a little freshly precipitated aluminium hydrate added to facilitate filtration (this is not always necessary), and the whole made up to 100 c.c. A portion of this solution is filtered, and the optical activity observed. The solution is then left in the cold until the next day, when another observation is taken in order to prove that inversion is complete. The cupric reducing power is also estimated.

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* We take this opportunity of making known the means we have now adopted for keeping a preparation of invertase as a hydrolytic agent. We have, in our former paper, given details of the preparation of the solution called yeast liquor. To this we add alcohol until the whole contains about 10—12 per cent. absolute alcohol. The mixture is allowed to stand a few days, and then the clear solution is filtered off. This solution is kept in a stoppered bottle, and it retains its inverting power indefinitely. It may either be used in its unaltered state or the invertase may be thrown out of solution by the addition of 3 or 4 times its own bulk of alcohol, and the syrupy precipitate, which immediately falls out, redissolved in water. We thus get, at a few minutes' notice, a fairly pure, and very strong solution of invertase.

† It is not necessary to determine both the optical activity and the cupric reducing power, as either factor by itself is sufficient. The optical activity will be found to be the more convenient, and, we think, the more accurate of the two, unless the solution is highly coloured.

‡ Brewers' yeast varies considerably in inverting power, but we think this amount is ample in most cases. The yeast need not necessarily be fresh, as it does not easily lose its power.

The method of calculating the results is the same as when invertase is used. The following formulæ will be found useful.

From the optical activity, the cane-sugar may be calculated as follows:—

$$P = \frac{\alpha - 2\alpha'}{m}.$$

α = the number of divisions indicated by the polarimeter scale for 200 mm. of the original solution.

α' = the same factor in the inverted solution.

m = the number of divisions of the polarimeter scale which 200 mm. of a solution containing 1 gram of cane-sugar per 100 c.c. alters on being inverted. In the case of the Soleil-Ventzke-Scheibler polarimeter which we use, 1 gram of cane-sugar in 100 c.c. indicates +3·84 div., whereas after inversion it gives −1·34 div. Therefore for our experiments $m = 5{\cdot}18$.

P = the weight of cane-sugar present in 100 c.c. of the original solution.

From the cupric reducing power we calculate the cane-sugar as follows:—

$$p = 0{\cdot}4308\left(2\frac{G'k'}{w'} - \frac{Gk}{w}\right).$$

G = the weight of 100 c.c. of the original solution.

G′ = the same factor for the inverted solution. Allowance must, of course, be made here both for dilution and for the 5 per cent. increase of the inverted sugar, but the latter number is so small that it need not be calculated accurately.

w = the weight of original solution used for the estimation.

w' = the same factor for the inverted solution.

k = the weight of cupric oxide reduced by w.

k' = the same factor for w'.

p = the weight of cane-sugar present in 100 c.c. of the original solution.

It is needless to remark that the values P and p should be identical within the limits of error of manipulation.

It will be seen from the description we have given that this method of estimating cane-sugar is quick and simple; it only remains for us to prove its accuracy. In the following experiments, we have compared it side by side with estimations made with a preparation of invertase; the accuracy of the latter method is, we believe, undisputed.

Exp. I.—A blank experiment to test whether the yeast itself imparts any optical activity to the solution. 1 gram pressed yeast was heated in 50 c.c. water to 55° for 4 hours. It was then filtered off by the aid of a little aluminium hydrate. The optical activity of the solution was 0·0 to −0·2 div. in 200 mm. It is obvious that the optical activity due to the yeast may be neglected.

Exp. II.—Estimation of cane-sugar in a hot water extract of malt.

Original solution. Sp. gr., 1079·7. Optical activity after heating to 80°, +67·4 div. in 100 mm. K of the solution diluted to twice its original bulk, 1·270 grams solution gave 0·1159 gram copper oxide.

Inversion was performed in 3 beakers; each contained 50 c.c. of the solution, and was treated exactly as we have described.

Beaker 1.—0·1 gram pressed yeast was employed. Optical activity after 4 hours +63·5 div., next day +63·2 div. in 200 mm. K, 1·320 grams solution gave 0·1405 gram copper oxide.

Beaker 2.—A solution of prepared invertase was used. Optical activity after 4 hours +63·2 div., next day +63·2 div. in 200 mm.

Beaker 3.—2·570 grams pure cane-sugar were added, and 0·2 gram yeast was employed. Optical activity after 4 hours +60·4 div., next day +60·0 div. in 200 mm. K, 1·274 grams solution gave 0·2020 gram copper oxide.

After making the calculations in the manner we have described, the results may be tabulated as follows:—

TABLE I.—*The Estimation of Cane-sugar in the Hot-water Extract of Mult.*

No.	Agent employed.	Cane-sugar added.	Results calculated on	Grams cane-sugar indicated by the	
				Optical activity.	K.
1	Yeast	none	100 c.c. of the solution	1·62	1·36
2	Invertase	none	” ”	1·62	—
3	Yeast	2·570	Amount added to the solution	2·52	2·34

It will be seen from this table that whilst the results calculated from the decrease of optical activity are perfectly satisfactory, those obtained from the increase in the cupric reducing power are not so good. This may be accounted for by the high reducing power of the original solution.

Exp. III.—Some treacle was dissolved in water with a little loaf sugar; the cane-sugar was then estimated as follows:—

Original solution. Sp. gr. 1054·2. Optical activity +18·9 div. in 100 mm. K, 2·312 grams solution gave 0·1124 gram copper oxide.

Beaker 1.—A solution of prepared invertase was used. Optical activity after 4 hours −6·1 div., next day −6·4 div. in 200 mm. K, 1·309 grams solution gave 0·1800 gram copper oxide.

Beaker 2.—0·4 gram pressed yeast was employed. Optical activity after 4 hours −6·4 div., next day −6·7 div. in 200 mm. K, 1·357 grams solution gave 0·186 gram copper oxide.

We have tabulated the results.

TABLE II.—*The Estimation of Cane-sugar in a Solution of Treacle, showing grams of Sugar in* 100 *c.c. of the Solution.*

Beaker.	Agent employed.	Cane-sugar indicated by the	
		Optical activity.	K.
1	Invertase	9·77	9·96
2	Yeast	9·88	9·92

The agreement between these four results is remarkable.

Exp. IV.—Some apples were finely divided and boiled in water. The solution was filtered off, and the cane-sugar estimated.

Original solution. Sp. gr. 1·024. Optical activity −11·3 div. in 200 mm.

Beaker 1.—A solution of prepared invertase was used. Optical activity the next day −7·2 div. in 200 mm.

Beaker 2.—0·1 gram yeast was used. Optical activity the next day −7·4 div. in 200 mm.

TABLE III.—*The Estimation of Cane-sugar in a Solution of Apple-juice, showing grams of Sugar in* 100 *c.c. of the Solution.*

Beaker.	Agent employed.	Cane-sugar indicated by the optical activity.
1	Invertase	0·60
2	Yeast	0·67

In this case the solution was too dilute to give perfectly accurate results, and, moreover, it was rather opalescent and difficult to see through.

The results of these experiments agree so well together, that no doubt remains as to the accuracy of the process. We may remark that these experiments were not picked out on account of the good results obtained, but were done by themselves specially to test the trustworthiness of the process.

In conclusion, we do not hesitate to say that the method we have described furnishes a simple and accurate means of estimating sucrose in *all* solutions.

VI.—*Action of Light on Pure Ether in Presence of Moist Oxygen.*

By A. RICHARDSON, PhD.

THE formation of an oxidising body in ether which has been exposed to the influence of light and air, was first observed by Schöbein (*Jour. Chem. Soc.*, **4**, 134), and subsequently this was identified with hydrogen peroxide, first by Dunstan and Dymond (*Pharm. J.*, **17**, 841), and afterwards by Berthelot (*Compt. rend.*, **108**, 543); and also by Poleck and Thümel (*Ber.*, **22**, 2863)—and myself (*Proc. Chem. Soc.*, 1889, 134). Recently, however, Dunstan and Dymond have published a paper (Trans., 1890, **57**, 574), in which they state that pure ether is not acted on by light when exposed in a moist atmosphere containing oxygen, and they consider that the formation of the peroxide is due to impurities contained in the liquid. In the paper above referred to, an abstract only of which was published (*Proc. Chem. Soc.*, 1889, 134), Dunstan and Dymond discuss my own experiments on the subject; the ether used in these experiments was obtained from so-called pure ether (prepared from rectified spirits); it was repeatedly shaken with water until the last traces of alcohol had been removed, then dried over calcium chloride, and repeatedly distilled from sodium until the metal was no longer acted on. Dunstan and Dymond, however, not having seen the original paper, consider that the means adopted to purify the ether used by me, as well as by other observers, were insufficient to preclude the possibility of the formation of hydrogen peroxide from impurities contained in the ether, rather than from the ether itself. I have, therefore, repeated my former experiments, using ether obtained from different sources, and purified by some of the methods suggested by them.

Experiments with Commercial Ether.

Commercially pure ether was taken, and all the alcohol removed by shaking about 30 times with water, the process being repeated until the washings failed to give the iodoform reaction. The ether was then shaken with a 4 per cent. solution of potassium dichromate acidified with sulphuric acid: after washing with water, it was treated with a solution of sodium hydrogen sulphite, shaken with potassium hydrate, and, lastly, washed with water and distilled; before exposure to light, the ether so prepared was without action on potassium iodide. Two quantities of this ether, of about 100 c.c. each, were exposed to light in bottles of colourless glass, containing also pure oxygen and water. After 11 days (July 13—24), the ether was tested with a solution of potassium iodide, to which it imparted a deep yellow coloration; shaken with a solution of potassium dichromate, the ether was coloured blue, thus proving the presence of hydrogen peroxide. Dunstan and Dymond, on the other hand, found that even methylated ether which had been purified in the manner above described was not affected by light, even after an exposure of five months.

Experiments with Ether prepared from Pure Alcohol and Pure Sulphuric Acid.

The ether prepared from the pure reagents was first shaken repeatedly with a solution of potassium hydrate and then with water till the washings failed to give the iodoform reaction. The ether so purified was treated as follows:—

(1.) About 200 c.c. of the pure substance was shaken with its own volume of potassium dichromate, every precaution being taken to follow exactly the method described by Dunstan and Dymond, and was distilled before being used. Samples of this ether, placed in bottles together with water and oxygen, were exposed to the influence of sunlight in a glass tank containing water, the temperature of which varied between 13·3° and 26·1°. In one experiment, air was substituted for oxygen above the liquid, the conditions being otherwise the same. Another bottle, containing ether and moist oxygen, was protected from the light by a covering of tin-foil, and was placed with the others in the tank, so that the heating effects were in all cases the same. After an exposure to light of 18 days (August 1—19), the contents of the bottles were examined; the ether which had been exposed to light gave with potassium iodide and with a solution of titanic acid a deep yellow colour, and potassium dichromate coloured the ether blue, whilst the ether which had been protected from the light was without action on these reagents.

(2.) The second method of purification consisted in the treatment of the ether with hydriodic acid; by this, as by the dichromate method, Dunstan and Dymond state that they were enabled to purify methylated ether so completely that after five months exposure to light it was without action on potassium iodide solution. A portion of the ether (about 100 c.c.) prepared from pure materials was, therefore, shaken repeatedly with about its own volume of a 3—4 per cent. solution of hydriodic acid, the method described by Dunstan and Dymond being again carefully followed. The ether, after distillation, was exposed to light in presence of moist oxygen, the bottle, as before, being immersed in water, the temperature of which ranged between 13·3° and 23°. After five days exposure (July 24—29), the ether was tested with a solution of potassium iodide, and gave a yellow colour, which grew darker on standing; it also imparted a yellow colour to a solution of titanic acid. Ether exposed under the same conditions, except that it was protected from the light, gave no reaction with these reagents.

(3.) The ether from the last experiments, amounting to about 200 c.c., containing hydrogen peroxide, was collected and again shaken with potassium dichromate, the process being repeated five or six times; the ether, which was coloured blue, was washed with sodium hydrogen sulphite and with potassium hydrate as before: after distillation, it was exposed with oxygen and water to a north light, so as to avoid direct sunlight, the temperature varying from 10° to 17·7°. Another sample was completely protected from the light, but otherwise exposed to similar conditions. After seven days (August 20—27), the ether was tested; that which had been exposed to light gave a yellow coloration both with potassium oxide and with titanic acid, whilst these reagents were not acted on by the ether which had been protected from the light.

Experiments with Ether prepared from a Second Sample of Pure Alcohol.

It was thought desirable to prepare a fresh quantity of ether from a new sample of absolute alcohol, which before use was allowed to stand over calcium oxide for 12 hours and then distilled; the ether obtained by the action of pure sulphuric acid on this alcohol was, as in the preceding experiment, shaken with potash and with water till all alcohol had been removed; it was then treated with potassium dichromate, dried over calcium chloride, and lastly over metallic sodium. The boiling point of this ether, amounting to 300 c.c., was determined with a thermometer graduated to 0·1°; it was constant throughout at 34·6° under a pressure of 760 mm. corrected to 0°. This result is identical with that found by Perkin and by Ramsay and Young, whilst the ether used by Dunstan and Dymond boiled at 35°, a somewhat higher temperature. A portion of this ether was exposed to a north light as in the preceding experiments, the temperature varying between 7·2° and 15·5°. After seven days exposure (September 29—October 6), the ether liberated iodine from potassium iodide, and a titanic acid solution was coloured yellow. An experiment was next made in which pure ether was exposed to the action of light at a low temperature, so that the heating effects might, as far as possible, be eliminated; this was done by surrounding the bottle containing ether and oxygen with water, which by the addition of ice was never allowed to rise above 2°. After exposure to light for four days, the ether was found to contain hydrogen peroxide. It appears, therefore, that the formation of this substance is brought about by light alone, independently of any heating effects.

From these experiments it will be seen that hydrogen peroxide was formed when ether, water, and oxygen were together exposed to light when the specimens of ether were prepared—(1) from the commercial "pure" product subsequently treated with potassium dichromate; (2) from pure alcohol and pure sulphuric acid, the product being afterwards treated with potassium dichromate or hydriodic acid; (3) from pure ether as in (2), in which hydrogen peroxide had been formed, but had been removed by further agitation with potassium dichromate; (4) from an entirely different specimen of pure alcohol and pure sulphuric acid, the ether being further purified with potassium dichromate, its purity being confirmed by the agreement of its boiling point with that obtained by other observers.

Dunstan and Dymond state that the formation of hydrogen peroxide in ether is the result of some unknown impurity, which can, however, be removed from even the methylated product by treatment with potassium dichromate; it might, therefore, be supposed that ether prepared with the utmost care from pure materials would after such treatment be freed from this substance, but, as has been shown, hydrogen peroxide is still formed in such a liquid after exposure to light, provided oxygen and water are present. Even on the supposition that the impurity escaped decomposition in the first instance, a second application of potassium dichromate should be sufficient to completely rid the ether of this body, but again it is found that hydrogen peroxide is formed in the ether after a few days exposure to light.

In no case have I been able to obtain a specimen of ether in which hydrogen peroxide is not formed after short exposure to light under the conditions above mentioned; and it would seem that the explanation of the discordant results obtained by Dunstan and Dymond and by myself is to be found, not in the supposition that my ether was impure, but in the conditions under which the ether was exposed to light in the two cases.

In the first place, one is led to enquire whether Dunstan and Dymond really had any oxygen above the ether in the bottle during exposure to light. For, although they describe minutely the nature and size of the bottles and the quantities of ether used, no allusion is made in their published paper to any precautions they may have taken to secure an atmosphere of oxygen or air in the space above the liquid. When ether is poured into a bottle, the vapour is evolved in such large quantities that the air is, to a great extent, expelled, and it is therefore open to doubt whether, if special precautions were not taken, sufficient oxygen was really present.

In one experiment made with the object of ascertaining whether oxygen has any action on ether (Trans, 1890, **57**, 577), these observers passed 200 litres of oxygen in the course of two days through ether heated nearly to its boiling point, and they remark that, although the ether was exposed to light during this period, no hydrogen peroxide was formed; two days exposure to light in a London laboratory would, however, hardly be sufficient to bring about the formation of a recognisable quantity of peroxide, even when oxygen is used.

In my own experiments, oxygen or air was in every case passed into the bottles immediately after the ether had been added; the stoppers were then inserted, and the bottles exposed to light in an inverted position, so that no gas could escape without first expelling the whole of the liquid. Again, it is to be noticed that Dunstan and Dymond used bottles of faintly greenish glass, which absorbs, to a considerable extent, the rays most influential in bringing about the formation of hydrogen peroxide. Lastly, it does not appear that they distilled the ether after treatment with potassium dichromate and sodium hydrogen sulphite, or after purification with hydriodic acid and sodium thiosulphate; traces of any of these reagents would be sufficient to decompose the minute quantities of hydrogen peroxide formed under the most favourable conditions. One is, therefore, led to suppose that the results obtained by Dunstan and Dymond, seemingly so diametrically opposed to my own, may possibly be due to one or more of the following circumstances:—

(1.) To the presence of ether vapour instead of oxygen above the liquid.

(2.) To the partial absorption by the glass of those rays which are most influential in bringing about the change in the ether.
(3.) To the presence of traces of reagents which decompose hydrogen peroxide.

Taking these points into consideration, it is not, perhaps, remarkable that their results do not agree with those of other observers, and they do not appear to be justified in concluding, as they do, that the experiments made by them "conclusively demonstrate that hydrogen peroxide cannot be formed from purified ether by exposing it to light, under ordinary atmospheric conditions in contact with air and water (*loc. cit.*, p. 584)."*

The experiments described by me show, on the contrary, that hydrogen peroxide is formed in pure ether, even after treatment with potassium dichromate or hydriodic acid, when exposed to light, provided—

(1.) That the ether vapour in the bottle is replaced by moist air or oxygen in the first instance.
(2.) That the bottles used are made of colourless glass.
(3.) That the last traces of the reagents used in its purification are removed.

Influence of Temperature on the formation of Hydrogen Peroxide in Ether.

The oxidation of ether at high temperatures has been investigated by Legler (*Ber.*, **14**, 602, **18**, 3343; *Annalen*, **207**, 381) and by Perkin (Trans., 1882, 41, 343), but it does not appear clear that hydrogen peroxide was amongst the products of decomposition obtained by these experimenters. It was also observed by Dunstan and Dymond (Trans., 1890, **57**, 585), that hydrogen peroxide was not formed when a mixture of ether vapour and oxygen was passed over strongly heated pumice; they, however, found that when cold water was in close proximity to the heated vapours, the peroxide was formed in considerable quantities. Although I have been unable to detect the presence of hydrogen peroxide in ether which has been kept in contact with moist oxygen in the dark, at ordinary temperatures, yet I have found that at comparatively low temperatures this substance was formed. Ether and moist oxygen were heated together in the dark at 60° for 40 hours; on testing the liquid, it was found that hydrogen peroxide had been formed to a considerable extent.

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* This, as Messrs. Dunstan and Dymond have since explained (Proc., 1890–91, p. 147), applies to the conditions under which the first series of experiments was performed, namely, diffused sunlight in London, and the electric arc-light. In the second series (Trans., 1890, 988), with intense sunlight in a clear atmosphere, hydrogen peroxide was formed in quantity sufficient to be detected by the chromic reaction. [EDITOR.]

Again, when a similar mixture was heated in the dark for four days to a temperature ranging between 78° and 88°, hydrogen peroxide was detected in the liquid; in these experiments, the quantities of ether taken were such that it was not entirely converted into vapour.

In a third experiment, the same quantity of ether as in the last case (contained in a sealed tube) was placed in a flask of 1000 c.c. capacity, which was filled with moist oxygen and sealed; the tube was then broken, and the mixture of ether and oxygen exposed to a temperature of 75—88°. Under these conditions, the whole of the liquid was converted into vapour; after four days heating, the contents of the flask were tested for hydrogen peroxide, and it was found that only an extremely minute trace of this substance was formed.

The experiments so far described throw no light on the question whether the hydrogen peroxide formed in presence of ether is a direct product of oxidation of water present, or is due to the oxidation of the ether. As this point is of considerable interest, the following experiments seem to show that the formation of the peroxide is due to the direct oxidation of the ether by light, as suggested by Berthelot, and that perfectly dry ether and oxygen give, after exposure, a compound which, on the addition of water, forms hydrogen peroxide.

Ether was dried by exposing it to a large surface of metallic sodium contained in one limb of a bent sealed tube, and after 11 days contact with the metal, a portion of the liquid was distilled into the other limb, which had been previously drawn out. It was then sealed off, and the distillate so obtained transferred to an outer tube, through which dry oxygen was drawn for four days; it was then sealed, and the inner tube broken. The mixture of ether and oxygen was tested after eight days exposure to light, and gave the hydrogen peroxide reactions with potassium iodide and with titanic acid. In a second experiment, the mixture of dry ether and oxygen was exposed in the dark to a temperature of about 70° for four days; in this as in the previous case, the liquid was found to contain hydrogen peroxide when tested with a solution of titanic acid.

If sodium is capable of removing completely the last traces of moisture from ether, the formation of hydrogen peroxide in these experiments is not due to the direct oxidation of water, as I had at first supposed; the results of other experiments, however, which are not yet completed, show that, under proper conditions, water itself is slowly oxidised under the influence of sunlight.

Note.—In a subsequent paper, Dunstan and Dymond have published the results of further experiments on this subject (Trans., 1890, **57**, 988), in which they state that hydrogen peroxide is formed by the action of sunlight on moist ether in presence of oxygen.

VII.—*Volumetric Estimation of Tellurium.* Part I.

By Bohuslav Brauner, Ph.D., Professor in the Bohemian University, late Berkeley Fellow of Owens College.

In my researches on tellurium (Trans., 1889, 382), I required a rapid and accurate process for its determination, but as all the known methods are gravimetric, and weighed filters have to be used, the results are not only liable to considerable errors, but also take a great deal of time and trouble.

As no volumetric methods for the estimation of tellurium have been published hitherto, I have devised and worked out some of this character, at first with a view to their technical application, but as the work progressed I studied the process, so as to develop it into an accurate volumetric method, and I now beg to lay the results I have obtained before the Society.

First Method.

Principle.—Solutions of tellurium dioxide in hydrochloric acid are reduced by stannous chloride, tellurium being precipitated, and stannic chloride formed.

a. $TeCl_4 + 2SnCl_2 = Te + 2SnCl_4$, or
b. $H_2TeO_3 + 2SnCl_2 + 4HCl = Te + 2SnCl_4 + 3H_2O$, or
c. $TeO_2 + 2SnCl_2 + 4HCl = Te + 2SnCl_4 + 2H_2O$.

The excess of reduced stannous chloride can then be determined by means of iodine solution volumetrically:

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI.$$

The method requires—

a. A solution of stannous chloride, prepared by boiling about 80 grams of granulated tin with 200 c.c. of hydrochloric acid, until hydrogen is no longer evolved, pouring off, adding some 450 c.c. of hydrochloric acid, and diluting to one litre. The solution is preserved in an atmosphere of carbon dioxide, and may be further diluted with water, according to the smaller or larger amount of tellurium which is to be determined.

β. A solution of about 7 grams of iodine and 10 grams of potassium iodide in 1 litre of water.

Determination.—The hydrochloric solution of tellurium dioxide is brought into a measuring flask of 100 c.c. capacity, and the stannous solution added while the liquid is warmed. At first a turbidity, consisting of finely divided tellurium, is produced, but, as soon as the stannous chloride is in excess, voluminous flocks of tellurium separate, and the liquid becomes perfectly limpid, especially after boiling. When the careful addition of stannous chloride no longer produces a precipitate, freshly boiled water is added up to the mark, the air in the neck of the vessel is displaced by carbon dioxide, by throwing in some sodium hydrogen carbonate, and the closed flask is cooled to the ordinary temperature by immersing it in water. While this is taking place, the relation between the stannous chloride and the iodine solution is determined in the usual way, using starch solution as indicator. When the flask containing the tellurium is cooled, it is filled up to the mark, the whole mixed, and the excess of stannous chloride determined in a measured portion of the clear liquid by means of iodine solution. It is convenient to filter the liquid through a folded filter, or Fessenden's modification of it (*Chem. News*, **60**, 102), in order to avoid the presence of finely divided tellurium, as this slowly decolorises iodine. The volume of iodine solution required for the whole 100 c.c. is calculated (neglecting the very small volume occupied by the tellurium, as the bulk of 1 gram of the latter is only 0·16 c.c.), and from this the amount of stannous chloride corresponding with it; on subtracting this from the stannous chloride originally employed, the volume of stannous chloride required for the precipitation of tellurium is found.

In order to ascertain whether the reaction between stannous chloride and a hydrochloric solution of tellurium dioxide* corresponds with the equations *a*, *b*, and *c*, given above, the following experiments were undertaken.

The filtrates obtained after precipitation of the tellurium were tested for it, but none was found; the precipitation under the given conditions may therefore be regarded as complete.

Starting with the relations of the iodine solution to the stannous chloride solution, and to a solution of a known weight of arsenious acid, the volumes of iodine and stannous chloride solutions, corresponding with a known weight of tellurium dioxide, were calculated, in accordance with the following proportion:—$As_2O_3 : 4I : 2SnCl_2 : TeO_2$. This supposes that the ratio of the quantity of iodine which is capable of converting 198 pts. of arsenious acid into arsenic acid is the same as the ratio of a quantity of stannous chloride necessary for the reduction of 159·6 grams of tellurium dioxide.

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* Such a solution, as long as it is concentrated, contains yellow tellurium tetrachloride, together with a hydrochloric solution of tellurous acid, which is colourless. The proportion of the latter increases on dilution, and at last the liquid becomes colourless.

Exp. 1.—A solution of sodium arsenite, containing 0·0495 gram As_2O_3 ($\frac{1}{4000}$ mol.), and equivalent to 0·0399 gram TeO_2 ($\frac{1}{1000}$ mol.), required 17·15 c.c. of iodine solution.

0·4803 gram of TeO_2 was dissolved in hydrochloric acid, and 55 c.c. stannous chloride solution added, 5 c.c. of which required 47·65 c.c. of iodine solution. 10 c.c. of the filtrate, the total of which was 100 c.c., required 31·65 c.c. iodine solution, and the total, therefore, 316 5 c c., this being equivalent to 33·17 c c. of the stannous solution, so that 55 − 33·17 = 21·83 c.c. stannous solution were used for the reduction of the tellurium oxide, coresponding to 208·0 c.c. iodine solution. As 17·15 c.c. of the last correspond to 0 0495 gram As_2O_3, and ought to correspond to 0·0399 gram TeO_2, the volume of stannous solution calculated for 0·4803 gram TeO_2 becomes 21·66 c.c, and that of iodine solution, 206·5 c c. This agrees as well with the 21·83 c.c. stannous solution, and 208·0 c.c. iodine solution actually employed, as could be expected, having regard to the different and indirectly comparable functions of the bodies entering into the reactions.

The second method of control was founded on the following more simple proportion:—$TeO_2 : 2SnCl_2 : 4I$.

Exp. 2.—0·4499 gram dry iodine, resublimed in the presence of potassium iodide, was dissolved in potassium iodide solution, and it was found that 32 42 c.c. of the stannous solution were required for its decolorisation, but 20 c c. of the same stannous solution were found equivalent to 36·6 c.c. of the empirical iodine solution, which therefore contains 0·27754 gram iodine in 36·6, or 0·0075833 gram in 1 c.c. As 126·85 parts of iodine are equivalent to 39·9 pts. of tellurium dioxide, 1 c.c. of the iodine solution represents 0 0023853 gram TeO_2. A solution of 0·1765 gram TeO_2 in hydrochloric acid was boiled with 11 c.c. of stannous chloride, and the excess of the latter was determined with iodine solution, of which 22·5 c.c. were required = 2·548 c.c. stannous chloride, as 1 c.c. stannous solution = 8·83 c.c. iodine solution, so that 11 − 2·548 = 8 452 c.c. stannous solution = 74·63 c.c. iodine solution were required for reduction. The weight of tellurium dioxide calculated from these data is 74 63 × 0·0023853 = 0·1780 gram, instead of the 0·1765 gram taken.

Exp. 3.—Another experiment of this kind yielded: Stannous solution = 11·0 c.c.; retitration with iodine = 23·15 c.c.; for reduction, stannous solution = 8·738 c.c. = 73·98 c.c. iodine solution = 0·17646 gram TeO_2, instead of the 0·1765 gram taken. Both these experiments show that the reaction between stannous chloride and tellurium dioxide really corresponds with the equations *a*, *b*, and *c*.

In actual practice the volumetric solutions were generally standardised by means of pure substances, the quantity of the latter being subsequently determined. In accordance with this principle, the following experiments were made, the relation between the stannous chloride and iodine solutions being as follows:—

Expts. 4— 7.. 1 c.c. $SnCl_2$ = 14·1 c.c. I = 0·02231 gram TeO_2.
„ 8—10.. 1 „ = 16·8 „ = 0·03931 „
„ 11—12.. 1 „ = 8·83 „ = 0·02089 „
„ 13—14.. 1 „ = 1·85 „ = 0·00431 „

No. of Experiment.	$SnCl_2$ added.	$I = SnCl_2$ back.		$SnCl_2$ for reduction.	TeO_2 taken.	TeO_2 found.
	c.c.	c.c.	c.c.	c.c.	grams.	grams.
4	25	79·5	5·63	19·37	0·4322	—
5	21	54·75	3 90	17·20	0 3815	0·3839
6	55	116·04	8·23	46·77	1·0436	1·0492
7	17	89·1	6·32	10·68	0·2348	0·2383
8	5	8·5	0·51	4·49	0·1765	—
9	14	163·1	9·43	4·57	0·1765	0·1797
10	6	26·0	1·55	4·45	0·1765	0·1750
11	11	22·5	2·55	8·45	0 1765	—
12	11	23·15	2·62	8·38	0·1765	0·1750
13	23	4·65	2·51	20·49	0·0883	—
14	25	7·85	4·24	20·76	0·0883	0·0895

Critical Remarks.

It will be seen from the above experiments that the results obtained by the stannous chloride method are sufficiently accurate for certain practical purposes. The following sources of error in this method must be noted, however.

The stannous chloride solution is very easily oxidised by the action of the oxygen of the air, so that its strength continually diminishes, especially during the boiling, cooling, and subsequent filtration, as shown by the following experiment:—

Exp. 15.—2 c.c. $SnCl_2$ solution, requiring originally 33·6 c.c. iodine solution, was diluted with water, boiled, and after cooling filled up to 100 c.c. Of this solution, 20 c.c. required 6·68 c.c. iodine solution;

the whole 100 c.c., therefore, would require 33·4 c.c. iodine solution After filtering, only 6·64 c.c. iodine were required for the 20 c.c. = 33·2 c.c. for the whole 100 c.c., so that the original strength, 2·00, becomes 1·99 in the first, and 1·98 in the second case. Owing to this source of error, the stannous chloride in excess will be found somewhat smaller, and the amount of tellurium dioxide correspondingly larger than it should be. A correction corresponding to the blank experiment may be introduced into the quantitative determination, although, if the method of comparison (see Exps. 4—14) be employed, this would be necessary only when the volume of the stannous chloride used varies within wide limits.

Other sources of error may also exist, although they cannot be ascertained with certainty. For instance, the tellurium probably carries down some tin with it as telluride, although this is doubtless difficult to prove. It seems, however, from the results obtained, that this source of error, as also the effect of the varying amount of hydrochloric acid present, does not affect the result seriously.

Application of the Method.

To show the application of the method just described, the basic sulphate of tellurium was analysed.

Exp. 16.—0·3198 gram of tellurium sulphate was dissolved in hydrochloric acid and precipitated with stannous chloride solution, of which 15 c.c. was used. Excess determined with 32·75 c.c. iodine = 3·39 c.c. stannous solution, so that 11·61 c c. stannous solution was used for reduction. As in Exp. 1, 0·4803 gram TeO_2 was indicated by 21·83 c.c. of the same stannous solution, the 11 61 c.c. = 0·25544 gram TeO_2. This gives for 100 parts of the salt—

	Calculated for Te_2O_4,SO_3.	Found.
TeO_2	79·95	79·88

Second Method.

Kessler (*Pogg.*, **95**, 204; **118**, 117) has shown that on the addition of chromic acid to hydrochloric solutions of arsenious or antimonious oxides, these are converted into arsenic and antimonic acids. A similar reaction might be expected to take place with a solution of tellurium dioxide, and it was supposed that the reaction would be the following:—

d. $3H_2TeO_3 + K_2Cr_2O_7 + 8HCl = 3H_2TeO_4 + 2KCl + Cr_2Cl_6$
$+ 4H_2O$, or

e. $3TeO_2 + K_2Cr_2O_7 + 8HCl = 3TeO_3 + 2KCl + Cr_2Cl_6 + 4H_2O$, or also

f. $3TeO_2 + K_2Cr_2O_7 + 4H_2SO_4 = 3TeO_3 + K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O$.

To a hydrochloric solution of tellurium dioxide, after dilution with water, potassium dichromate solution was added in excess, and after some time the excess of dichromate was determined by means of a solution of ammonium ferrous sulphate, which was added until a drop of the solution brought into a fresh dilute solution of potassium ferricyanide gave a distinct blue coloration. The relation between the dichromate and the ferrous solution was determined in the same manner.

A series of experiments was first made, in order to see whether the reaction between tellurous and chromic solutions corresponded with the above equations *d*, *e*, and *f*.

2·5 grams of potassium dichromate was dissolved in 1 litre of water, and 10 c.c. of this solution were found to oxidise 2·83 c.c. of the ferrous solution.

Exp. 17.—0·048 gram arsenious acid was dissolved in sodium carbonate, and the solution then acidified with hydrochloric acid. The solution was found to require for oxidation 18·63 c.c. $K_2Cr_2O_7$ solution, which corresponds with 0·07738 gram TeO_2, for 198 parts of As_2O_3 (1 mol.) are oxidised by the same quantity of dichromate as 319·2 parts of TeO_2 (2 mols.). The 0·0737 gram of TeO_2 used for the experiments below ought to require 17·3 c.c. of $K_2Cr_2O_7$ solution.

Exp. 18.—0·1064 gram pure iron was dissolved in dilute sulphuric acid, and 35·95 c.c. of the chromic solution was used for its oxidation. According to the equation

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O,$$

336 parts Fe (6 atoms) and 478·8 parts TeO_2 (3 mols.) require one and the same quantity of dichromate for oxidation, so that 1 c.c. of the above chromic solution indicates 0·004218 gram TeO_2, and 0·0737 gram TeO_2 should require 17·5 c.c. dichromate solution.

The strength of the dichromate solution may also be calculated from the quantity of dichromate contained in it. As 295·36 parts $K_2Cr_2O_7$ (1 mol.) oxidise 478·8 parts TeO_2 (3 mols.), 1 litre of the solution, containing 2·5 grams $K_2Cr_2O_7$, oxidises 4·1493 grams TeO_2, so that 0·0737 gram TeO_2 requires 17·8 c.c. The following first series of approximate results was obtained:—

No. of experiment.	$K_2Cr_2O_7$ added.	$\underbrace{FeSO_4 = K_2Cr_2O_7.}_{\text{back.}}$		$K_2Cr_2O_7$ for oxidation.	H_2O present	HCl present.	H_2SO_4 1/1 present.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
19	35	4·6	−16·3	19·7	100	20	—
20	35	4·4	−15·5	19·5	10	—	10
21	36	4·7	−16·4	19·6	10	—	10
22	40·5	5·9	−20·7	19·8	100	10	—
23	40	5·7	−20·0	20·0	100	—	10
24	40	5·7	−20·0	20·0	100	20	—
25	20	1·0	− 2·8	17·2	200	10	—
26	20	0·7	− 2·5	17·5	200	10	—

The duration of interaction between the chromic and tellurous solutions was one hour in Experiments 18, 19, 20; 16 hours in 21, 22, 23; two minutes in 24; and five minutes in 25.

Another solution containing 0·1096 gram TeO_2 would require, when calculated from the quantity of dichromate dissolved, 26·4 c.c. of dichromate solution.

No. of experiment.	$K_2Cr_2O_7$ added.	$\underbrace{FeSO_4 = K_2Cr_2O_7.}_{\text{back.}}$		$K_2Cr_2O_7$. for oxidation.	H_2O present.	HCl present.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
27	18	1·3	−2·3	15·7	100	—
28	30	2·4	−4·5	25·5	100	10
29	20	1·8	−3·3	16·7	100	10
30	25	0·1	−0·2	21·8	100	10
31	30	2·4	−4·0	25·6	100	10
32	30	1·9	−3·4	26·6	100	10
33	30	1·9	−3·4	26·6	100	10

Duration of experiments:—Experiment 27, 2 min.; 28, 15 min.; 29, 2 min.; 30, 10 min.; 31, 15 min.; 32 and 33, 24 hours.

A solution of 0·0828 gram TeO_2, requiring 20·0 c.c. $K_2Cr_2O_7$, was used in the following experiments:—

No. of experiment.	$K_2Cr_2O_7$ added.	$\underbrace{FeSO_4 = K_2Cr_2O_7.}_{\text{back.}}$		$K_2Cr_2O_7$ for oxidation.	H_2O present.	HCl present.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
34	30	5·6	−10·0	20·0	100	3
35	30	5·6	−10·0	20·0	100	10
36	30	5·8	−10·2	19·8	100	3
37	30	5·6	−10·0	20·0	100	10
38	30	5·7	−10·1	20·1	100	20
39	30·2	5·6	−10·0	20·2	100	30

Duration of experiments:—Experiments 34 and 35, 24 hours; 36, 37, 38, and 39, 10—15 minutes.

From these experiments, the first series of which is only approximately accurate, it will be seen that the oxidation of tellurous acid is the more complete, the longer the action of the dichromate, the larger the volume of the dichromate solution added, and the larger the quantity of hydrochloric acid present. In sulphuric acid solution, the reaction corresponds with the equation *c*, but requires more time than in hydrochloric solution.

The last series of experiments was made with a standard solution of pure potassium dichromate. The purest commercial salt was purified by fractional solution in and disturbed crystallisation from water, the middle portions only being used. 2·5936 gram ($\frac{1}{100}$ mol. weight) was dissolved in water and diluted to 1 litre, 1 c.c. of the solution indicating 0·004788 gram TeO_2 ($\frac{3}{100}$ mol. weight). 3·1880 grams TeO_2 was dissolved in 50 c.c. of hydrochloric acid and diluted to 100 c.c., so that 5 c.c. of the solution taken for each experiment contained 0·1594 gram TeO_2. In each experiment, 20 c.c. concentrated hydrochloric acid was added, and water to make up the total volume to 100 c.c. The volume of the dichromate solution was nearly equal in all the experiments, so that the whole series of experiments was carried on under precisely similar conditions, except that the duration of the action was varied, as seen from the last column. The volume of dichromate solution necessary for the complete oxidation of 0·1594 gram TeO_2 is = 33·3 c.c.

No. of experiment.	$K_2Cr_2O_7$ added.	$FeSO_4 = K_2Cr_2O_7$ back.		$K_2Cr_2O_7$ for oxidation.	Time.	
	c.c.	c c.	c.c.	c.c.	h.	m.
40	43·4	13·9	−23·1	20·3	0	1
41	40·0	10·7	−17·8	22·2	0	2
42	40·4	6·1	−10·4	30 0	0	7
43	40·4	4·9	− 8·2	31·8	0	10
44	40·0	4 5	− 7·5	32·5	0	17
45	40·0	4·4	− 7·3	32·7	0	30
46	40 0	4·3	− 7·2	32·8	1	0
47	41·0	4·9	− 8·2	32·8	1	15
48	40·5	4·4	− 7·3	33 2	3	50
49	41·0	4·7	− 7·7	33·3	5	40
50	40·5	4·2	− 7·1	33·4	18	0
51	40·0	4·0	− 6·6	33·4	18	0
52	40·0	3·8	− 6·3	33·7	25	0

On graphically representing the data obtained in this series by a curve, the volumes of dichromate solution standing as ordinates and the time of interaction as abscissæ, a very regular hyperbola, running through the points, is obtained, as seen from the Plate.

Critical Remarks.

The hyperbola, on reaching the point $y = 33{\cdot}3$, does not take a direction parallel to the axis x, but rises slowly further on, but as after one hour's action almost all the tellurous acid is converted into telluric acid, a secondary reaction may be assumed to take place. The experiments were made at a summer temperature of 25—30°, and a feeble, peculiar odour, like that of chlorine or ozone, was observed after some time, which must be due to the action of the mixture of chromic and telluric acids on the hydrochloric acid, as chromic acid alone in the presence of hydrochloric acid is found to require the same amount of ferrous solution for titration after 24 hours as immediately after mixing.

The mixture of chromic and telluric acids, therefore, will require less ferrous solution, and the quantity of chromic solution required for oxidation will be found somewhat larger. The secondary reaction may take place in the following two phases:—

g. $H_2TeO_4 + 2HCl = H_2TeO_3 + Cl_2 + H_2O$, and
h. $3H_2TeO_3 + K_2Cr_2O_7 + 8HCl = 3H_2TeO_4 + 2KCl + Cr_2Cl_6 + 4H_2O$.

The observed rise of the hyperbola may be due to this reaction.

Another source of error is due to the fact that the blue coloration with potassium ferricyanide, which is produced when all the chromic acid has been destroyed by the ferrous sulphate solution, appears distinctly only when 100 c.c. of the solution contains an excess of 0·4—0·5 c.c. ferrous solution. On applying this correction to the process of determining the relation between the ferrous and chromic solutions, as well as to the final titration of the tellurous solution, the result is very considerably influenced.

Uncorrected:—20 c.c. $K_2Cr_2O_7$ = 12·07 c.c. $FeSO_4$, and 41 c.c. $K_2Cr_2O_4$ — (4·65 c.c. $FeSO_4$ = 7·7 c.c. $K_2Cr_2O_7$) = 33·29 c.c. $K_2Cr_2O_7$.

Corrected:—20 c.c. $K_2Cr_2O_7$ = 11·62 c.c. $FeSO_4$, and 41 c.c. $K_2Cr_2O_7$ — (4·20 c.c. $FeSO_4$ = 7·23 c.c. $K_2Cr_2O_7$) = 33·77 c.c. $K_2Cr_2O_7$.

The correction which must be applied to the volume of chromic solution used for oxidation is +0·5, and we see that according to this the theoretical quantity of 33·3 c.c. $K_2Cr_2O_7$ is required after an interaction of one hour. But it is uncertain whether one and the same correction can be applied both in standardising and in making the final experiment.

As the reaction between tellurium dioxide and chromic acid in

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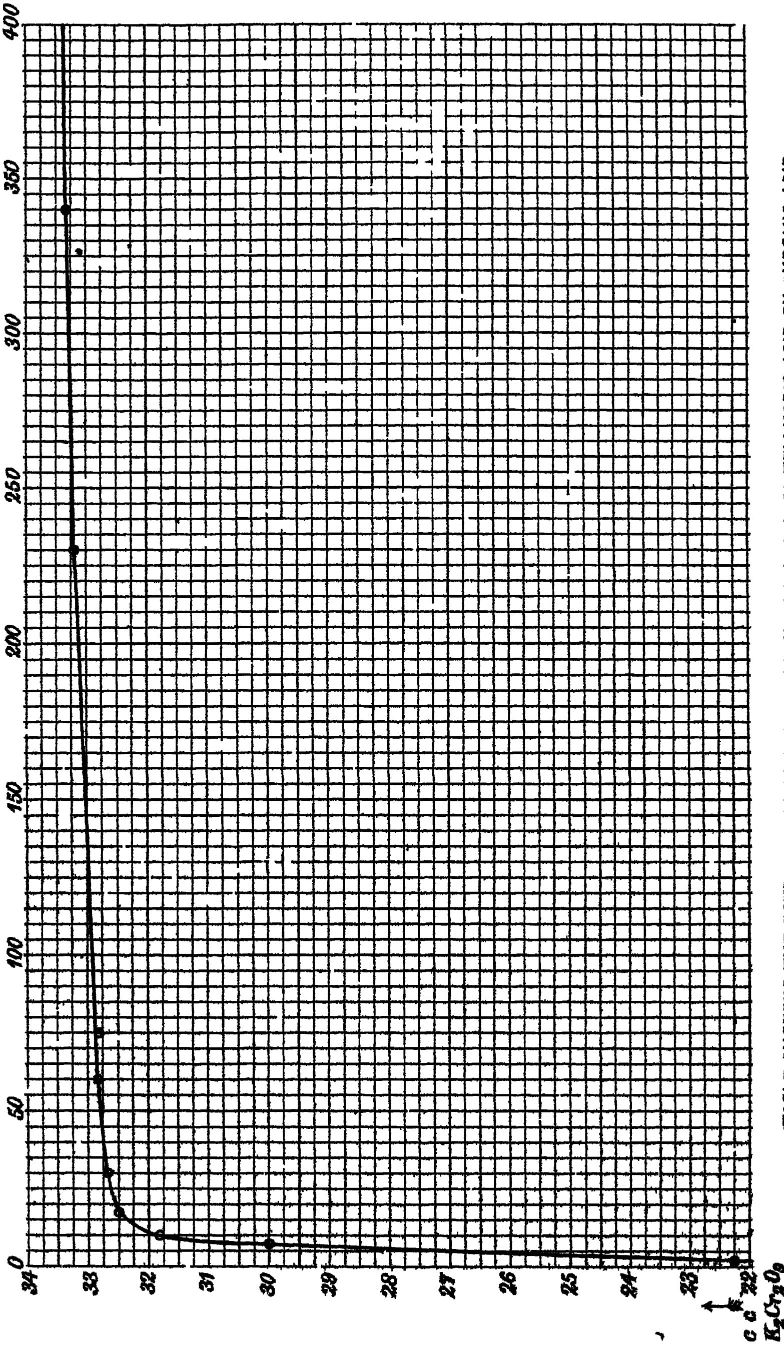

TABLE SHOWING THE RATE OF CONVERSION OF TELLUROUS ACID INTO TELLURIC ACID BY CHROMIC ACID

hydrochloric acid solution requires at least one hour for completion, it is perhaps rather of theoretical interest than useful as a practical volumetric method.

Further volumetric methods for the determination of tellurium will be described in a future paper.

VIII.—*Note on Dibenzanilide.*

By J. B. Cohen, Ph.D., Owens College, Manchester.

The researches of Paal and Otten (*Ber.*, **23**, 2587), and of Pictet (*Ber.*, **23**, 3011), which have recently appeared, induce me to publish the following observations, which I made some time ago. In the latter portion, I was greatly assisted by Mr. F. Brownsword, B.Sc., a former student in this laboratory.

When a mixture of phenylthiocarbimide with benzaldehyde is heated for some hours at 190°, sulphuretted hydrogen is evolved, and several products are formed. These consist mainly of benzanilide and benzaldehyde-aniline, and form a semi-solid mass from which the benzanilide may be isolated by filtration. The latter was recrystallised from alcohol and melted at 161—162°. When heated in a sealed tube with concentrated hydrochloric acid, it splits up into aniline and benzoic acid. The following result was obtained on analysis:—

0·1995 gram gave 12·4 c.c. of N at 16·5° and 761·2 mm.

	Found.	Calculated.
N........	7·36	7·10

The reaction is a complex one, and was not studied further. A similar reaction described by Losanitsch (*Ber.*, **6**, 176), and repeated by Higgin (Trans., 1882, 132), consists in heating phenylthiocarbimide with benzoic acid at 220°. A solid product melting at 160° is thus formed, which is stated to be *dibenzanilide;* but in neither paper is any analysis given. The similarity of the two reactions, and the alleged difference in the product obtained, induced me to repeat Losanitsch's experiment. The product of the reaction is a solid, crystalline mass, which, when recrystallised from alcohol, melted at 161—162°.

The following result was obtained on analysis:—

0·2150 gram gave 13·4 c.c. of N at 13·4° and 775·5 mm.

	Found.	Calculated for benzanilide.	Calculated for dibenzanilide
N........	7·60 per cent.	7·10	4·63

The compound is obviously benzanilide.

In this as in all subsequent analyses, the nitrogen alone has been determined, as this suffices to establish the identity of the compound with benzanilide or dibenzanilide.

To confirm the above result, and to compare the product with dibenzanilide, I attempted to prepare the latter by the method of Gerhardt and Chiozza (*Ann. Chim. Phys.* [3], **46**, 129) by heating a mixture of benzanilide and benzoyl chloride in molecular proportion at 160—180°. In doing so, I followed in detail the method of Gerhardt and Chiozza; but was entirely unsuccessful in obtaining dibenzanilide.* The substance was purified by the method given in their paper, namely, by digesting with sodium carbonate solution. washing with water, and recrystallising the product from alcohol. Prepared in this way, the compound obtained is a white, granular mass consisting of aggregates of microscopic crystals, differing entirely in appearance from the glistening plates of benzanilide. The substance, which was evidently impure after two recrystallisations, melted at 158°, and gave the following results on analysis :—

1. 0·2020 gram gave 13·1 c.c. of N at 24° and 759·9 mm.
2. 0·2168 „ „ 14·2 „ „ 15·5 „ 747·8 „

	Nitrogen found.
1	7·54 per cent.
2	7·64 „

The above process was then repeated under a variety of different conditions. The mixture of benzanilide and benzoyl chloride was heated at 200°, 220°, and 230° for different periods from 3 to 12 hours, and also in sealed tubes at 180°.

In the latter case, it may be mentioned that no excess of pressure was observed on opening the tubes. This would prove that no great evolution of gas had occurred during the heating. In the many analyses made of both the impure and purified product, in not one instance did the percentage of nitrogen fall below 7 per cent.

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* The authors state that gaseous hydrogen chloride is evolved during the reaction, but this is not the case. The evolution of hydrogen chloride is not more apparent than when benzoyl chloride alone is heated at the same temperature in an open vessel, as I observed by placing benzoyl chloride in a flask in the same bath with the mixture. There was no marked evolution of gas in either case. Gerhardt and Chiozza obtained, as a result of one analysis, 5 per cent. of nitrogen in place of 4·6 per cent. The percentage, which I recalculated from their figures, should be 5·22 per cent. This is undoubtedly due to the fact that the benzanilide, which remains unaltered in the process, contains benzoic acid, from which it is exceedingly difficult to free it. The low melting point (137°) may also be accounted for in this way.

The following are some of the results of the analyses of the products obtained at 180°.

1. 0·2170 gram gave 13·4 c.c. of N at 16° and 750 mm.
2. 0·2068 „ „ 12·65 „ „ 12·9° „ 739·85 mm.
3. 0·2160 „ „ 13·4 „ „ 13·5° „ 750·9 „

	Per cent. of N found
1. After heating in a sealed tube for 4 hours at 180° and crystallising the product three times. Melting point 158°	7·19
2. After heating at 180° for 4– 5 hours and crystallising once	7·13
3. After heating at 180° for 4—5 hours and crystallising three times	7·34

The following experiment was then carried out:—45 grams of pure benzanilide melting at 160—160·5° were heated at 180° with 34 grams of benzoyl chloride for five hours, and the liquid product poured whilst hot into a large volume of cold water. To prevent possible decomposition of dibenzanilide, the product was digested with sodium carbonate solution in the cold, by adding, successively, small quantities of a solution of sodium carbonate until an alkaline reaction remained permanent. It was then filtered, dried, and weighed. 43 grams were obtained. The substance was then submitted to a process of recrystallisation from alcohol, and the melting point of each product determined as follows:—

First Crystallisation.—Granular mass, m. p. 155°, also a minute quantity of needle-shaped crystals melting at 156°.

Second Crystallisation.—White grains, m. p. 157—158°. A few needle-shaped crystals again formed and were carefully separated. These melted at 157°.

Third Crystallisation.—Appearance similar to the previous product, m. p. 157—158°. No needles were present.

Fourth Crystallisation.—Appearance unchanged, m. p. 157—159°. No needles.

Fifth Crystallisation.—The crystals were more distinctly tabular, and had the characteristic glistening appearance of benzanilide, m. p. 157—159°.

By evaporating the mother liquors from the separate crystallisations, more granular crystals mixed with a brown resinous matter separated, and from the last mother liquor, a small amount of benzoic acid was obtained. The presence of benzoic acid is not easy to explain. The amount of brown, resinous matter increases with the temperature at which the reaction is carried out. In an experiment made at 230°, the product was very impure from this cause, and after five crystallisations from alcohol, only melted slowly at 140—151°. Under these conditions, the percentage of nitrogen in the compound was always *above* the calculated amount.

The quantity of the needle-shaped crystals was too small to allow me to do more than make a determination of the melting point. I attempted to obtain more of them by evaporating the mother liquors and dropping some of the needles into the solution to bring about crystallisation. On the assumption that benzanilide might be dimorphous, I also added a crystal or two to a saturated solution of pure benzanilide. In both cases I was unsuccessful in obtaining the needles. This compound may therefore be dibenzanilide.

The literature of the subject would be incomplete without reference to the work of Steiner on tribenzhydroxylamine (*Annalen*, **178**, 235). The author states that by heating α-tribenzhydroxylamine in a closed tube, dibenzanilide is formed and carbon dioxide evolved. The evidence for this is based on the decomposition of about 1 gram of substance, which gave a volume of gas roughly corresponding to the amount required by the decomposition of the substance in the manner indicated. He admits that the product does not resemble dibenzanilide, that it does not smell of phenyl cyanate; but possesses a strong odour of bitter almonds, and is to a great extent soluble in cold ether. The residue insoluble in ether, after crystallisation, formed small needles with the melting point 161°. Steiner, finding that the melting point did not agree with that of Gerhardt and Chiozza's compound, repeated their experiment of heating together benzoyl chloride and benzanilide. The product, after recrystallisation, had the required melting point of 161°. The analysis gave 5·38 per cent. of nitrogen in place of 4·63 per cent. Like Gerhardt and Chiozza, Steiner probably obtained benzanilide containing benzoic acid.*

The author concludes by stating that the products of decomposition of α-tribenzhydroxylamine "are not wholly, apparently not even to any extent, dibenzanilide and carbon dioxide."

We may then conclude that, up to the present, dibenzanilide has not been prepared, at any rate not in the pure state. The synthesis of this compound I desire to reserve for future study.

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* This experiment was again repeated in 1882 by Higgin (Trans., 1882, 132), at a temperature of 230°. The author obtained needles melting at 136°, but as he only determined the percentage of carbon in the compound, viz., 79·60 (benzanilide has 79·18 and dibenzanilide 79·73 per cent.), no satisfactory conclusions can be drawn.

Paal and Otten, as well as Pictet, point out in the papers referred to at the beginning of this note, that by the action of benzoyl chloride on acetanilide, benzanilide and acetyl chloride are formed in theoretical quantities, and, from this and other experiments, state that, in this reaction, the acid chloride of higher molecular weight replaces that of lower molecular weight in combination with the amine. I had occasion incidentally to try and replace the amido-hydrogen atom in benzanilide by acetyl, and attempted this by heating benzanilide with acetic anhydride and a small quantity of fused sodium acetate. The benzanilide was converted into acetanilide which melted at 112°. It appears, therefore, that under these conditions the action is reversed. I intend to try this reaction with the other homologues of benzanilide.

This is an additional confirmation of the fact that the replacement of the second amido-hydrogen atom by an acid radical in aniline is not readily accomplished by the ordinary methods.

IX.—*Phenylbromacetic Acid, an apparent Exception to the Le Bel-Van't Hoff Hypothesis.*

By T. H. Easterfield.

Van't Hoff, in his "Dix Années dans l'Histoire d'une Théorie," after referring to the reservations which accompanied the introduction of his fundamental idea, expresses his views in the following sentence ("Dix Années," p. 49):—"Or depuis lors la découverte de l'activité chez l'iodure de l'alcool amyl secondaire $CHI{\cdot}CH_3{\cdot}C_3H_7$, par M. le Bel, a prouvé que même la différence entre l'hydrogène et un atome halogène suffit à la production du pouvoir rotatoire; depuis lors il paraît que toute restriction a perdu sa raison d'être." Up to the present time, however, this amyl iodide of le Bel appears to stand alone as the only active compound in which we have reason to believe that a halogen is united to the asymmetrical carbon. It therefore seemed desirable that similarly constituted haloïd derivatives should be prepared and studied. Accordingly, at the suggestion of Professor Emil Fischer, I have attempted to prepare other active substances of the type alluded to, and although the results obtained so far are only of a negative character, they may perhaps possess sufficient interest to excuse their presentation before the Society.

Active mandelic acid was chosen as the parent substance; it was prepared from amygdalin according to the directions given by Lewkowitsch (*Ber.*, **16**, 1565); 1 gram of the acid was sealed up in a tube with 10 to 15 times its weight of fuming hydrobromic acid saturated at 0°. The mandelic acid rapidly dissolved, yielding a clear solution. The tube was now placed in a water-bath at 50° and maintained at that temperature for two hours; at the end of that time the mandelic acid had become transformed into phenylbromacetic acid, $C_6H_5 \cdot CHBr \cdot COOH$, most of which had separated as a light brown oil; this solidified on cooling, and after recrystallisation from boiling light petroleum showed a melting point of 78—80°. The alcoholic solution of the brominated acid was absolutely inactive; the melting point of the acid corresponds with that of the inactive brominated acid prepared from inactive mandelic acid by the same process. On gently warming the acid with dilute soda solution, acidifying, and extracting with ether, it yielded inactive mandelic acid melting at 118°.

Similarly, phenylchloracetic acid, prepared by the action of hydrochloric acid on active mandelic acid, was found to be inactive and to correspond in melting point and general character with the inactive synthetical acid. With fuming hydrochloric acid, however, a temperature of 95—100° was necessary in order to start the reaction. It was not found possible to prepare an active chlorinated acid by the action of phosphorus pentachloride on an ethereal solution of active mandelic acid.

Fuming hydriodic acid appears to have no action on mandelic acid at low temperatures; at the temperature of the laboratory in summer, reduction took place gradually, no iodo-acid being formed.

The resolution of the halogenated acids by means of the alkaloïd salts was also attempted but without success; the chlorinated and brominated acids are slowly decomposed even by cold water, and the alkaloids at once remove the halogen atom. The difficulty of finding a suitable solvent prevents these substances being submitted to the action of organised ferments. These remarks apply equally to bromosuccinic acid, with which some experiments were tried.

Kekulé (*Annalen*, **130**, 21) has prepared bromosuccinic acid by the long-continued action of hydrobromic acid on active malic acid at 100°. Here again the brominated acid was inactive, and yielded inactive malic acid on treatment with moist silver oxide. Kekule remarks that it would have been only reasonable to expect an active brominated derivative .to have been formed under these circumstances; and surely the same remark holds good in the case of the reaction between hydrobromic and active mandelic acids at so low a temperature as 50°. In the case of malic acid, it may indeed be supposed that maleïc acid has been first formed, that this has been converted into fumaric acid, and has then taken up the elements of hydrobromic acid to form the inactive bromosuccinic acid; such an assumption is impossible in the case of mandelic acid.

It would be indeed rash to generalise from the few facts before us, but the possibility certainly seems to suggest itself that such strongly negative radicles as chlorine and bromine cannot be introduced by substitution into an asymmetrical active group without destroying the activity of the molecule. This might be due either to the fact that there is something in the nature of these atoms themselves which prevents activity in their compounds, or what is perhaps more likely, because the introduction of so chemically potent an atom produces such a disturbing effect on the whole molecule that a general re-arrangement of its atoms becomes necessary; in other words, that intramolecular change takes place.

The above investigation was carried out in the laboratory of the University of Wurzburg. I take this opportunity of expressing my deep indebtedness to Professor Fischer for the characteristic kindness which I have received at his hands.

X.—*Action of Heat on Nitrosyl Chloride.*

By J. J. Sudborough, B.Sc. (Lond.), A.I.C. (Associate of the Mason College), and J. H. Millar.

It is well known that nitric peroxide, N_2O_4, begins to dissociate at temperatures just above the boiling point of the liquid. When the gas is heated, dissociation into nitrogen dioxide is far advanced, according to Playfair and Wanklyn at a temperature of 97·5°, and is complete, according to Deville and Troost, at 140° (*Compt. rend*, **64**, 237). Richardson has studied the action of heat upon this compound at higher temperatures, and has found that at 620° nitrogen dioxide is completely dissociated into nitric oxide and oxygen (Trans., 1887, **51**, 397).

We determined to examine the action of heat in like manner upon nitrosyl chloride, the only known oxychloride of nitrogen, as it seemed probable that it would dissociate into nitric oxide and chlorine more readily than nitrogen dioxide splits into nitric oxide and oxygen.

To elucidate this point, we undertook several series of experiments, of which this paper contains a brief account.

Preparation of Nitrosyl Chloride

As a means of preparing the chloride, we invariably used nitrosyl sulphate (chamber crystals) and sodium chloride. The sulphate we obtained by passing the red gas evolved from copper and nitric acid or white arsenic and nitric acid into sulphuric acid. The red fumes were first passed through a Liebig condenser with a Woulff's bottle attached, so as to condense any nitric acid which might pass over, and all traces of moisture were removed by interposing a calcium chloride tube. The purified gas was then passed into the sulphuric acid. That these precautions were necessary was proved by the fact that our first sulphate—prepared by merely passing the nitrous fumes into sulphuric acid without previous drying—contained a small amount of nitric acid, and the chloride prepared from it always contained traces of nitrogen peroxide and hydrochloric acid, the former of which was readily detected by its absorption spectrum.

When the nitrous fumes had been passed into the sulphuric acid for some eight or nine hours, small crystals of nitrosyl sulphate appeared; the reaction was then stopped, as the sulphate in a semi-liquid form was much more convenient. The sodium chloride used was merely common salt thoroughly dried. The two salts were mixed together in a Wurtz's flask, and the nitrosyl chloride, which was evolved on gently warming, was passed through a calcium chloride tube.

That the gas thus evolved was practically pure nitrosyl chloride, was proved by estimating the amount of chlorine in a given weight of the gas.

Vapour Density at Ordinary Temperatures.

The vapour density of nitrosyl chloride at ordinary temperatures had been previously determined by Tilden (*Journ. Chem. Soc.*, 1874, 27, 632). From his results, it was clearly established that the molecule of the gas at ordinary temperatures is represented by the formula NOCl, and not by any multiple of this.

Density found.	Calculated for NOCl.
33·25	32·67

Our investigations consisted of determinations of the vapour density at temperatures ranging from 15° to 985°. Where possible, the density was obtained by weighing the gas, and checked by estimating the chlorine; but, in some cases, we had to rely merely on the amount of chlorine found in order to calculate the density.

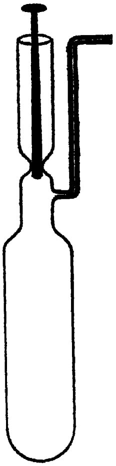
In order to fill the bulbs with the gas, we used one of the two following methods :—

(1.) Condensing the gas by placing the bulb in a freezing mixture, till several cubic centimetres of the liquid were formed, and then allowing it to boil off (b. p. —8°). In this case, we found it very requisite to have the bulb perfectly dry, and to have the outlet tube as far removed from the freezing mixture as possible, as the moisture which condensed around the cold tube readily decomposed the chloride as it passed into the air, and the nitrous and hydrochloric acids thus formed would readily find their way back into the bulb.

(2.) By passing the gas through a bulb open at both ends till all the air was expelled. We usually let the gas pass through for from 30 to 45 minutes.

Sulphuric Acid Bath.

Our first set of experiments was made at temperatures between 15° and 165°. The method used was that of condensing the gas in the tube. The kind of tube we found most convenient, both for fitting in the bath and also for obtaining the liquid free from moisture, is that represented in the figure.



The bulb had two openings, the larger one, which was wide enough to allow an ordinary piece of glass tubing to pass down, was ground, and had a glass stopper to fit, whilst the smaller one consisted of a long narrow capillary. The gas was passed in through the wide neck by means of a piece of glass tubing which reached to the bottom of the bulb. When a quantity of liquid was condensed, the neck was stoppered, and a cap placed over the end of the capillary. The bulb was cleaned, and the cap removed. It was then put into the sulphuric acid bath, which was large enough to cover the bulb up to the stopper. The temperature was slowly raised, and the bath kept at the required temperature for 10 minutes. The cap was then replaced, the bulb removed, cleaned, and inverted in distilled water; the cap was removed, and the water allowed to enter. The solution thus obtained was mixed with excess of ammonia, and evaporated on the water-bath to dryness in order to get rid of all nitrite; the residue was then dissolved, and the solution titrated with decinormal solution of silver nitrate. From the amount of chlorine found, the vapour density was readily determined.

Three determinations made in this way at 15° gave a mean result of 32·5. The density according to theory is 32·67.

Experiments conducted in the same way at 65°, 115°, and 165° gave results which showed that no dissociation had taken place. In all cases, the density came out above 32.

Bath of Methyl Salicylate Vapour.

We next proceeded to heat the gas in a bath of methyl salicylate vapour, the temperature of which was 222°. In this set of experiments, the gas was allowed to pass through the bulb for about 45 minutes. The bulbs used were merely large boiling tubes of about 150 cubic centimetres capacity drawn out at both ends into fine long capillaries. When the gas had passed through for the allotted time, one end was sealed off; the bulb was then lowered into the bath, and the open end allowed to project through the cork; this open end was fitted with a smaller bulb containing nitrosyl chloride, in order to prevent diffusion during the experiment. The salicylate was then boiled, and after the bulb had been in the vapour for about 10 minutes, the open end was sealed off. The bulb was then removed, allowed to cool, and weighed; and from this weight the density was calculated. The end of the capillary tube was afterwards broken off under water, the chloride dissolved, and the chlorine estimated as before; this served as a check on the density determined by weighing. Three experiments were conducted at this temperature; the resulting density was 32·3, thus indicating that no dissociation had taken place.

Bath of Sulphur Vapour.

Our next experiments were conducted in a bath of sulphur vapour. The vessel in which the sulphur was boiled was not of very large dimensions, and consequently the vapour became superheated. It was, therefore, necessary to determine the temperature by means of an air thermometer. This was readily done by taking a dry bulb of approximately the same size as the one used for the nitrosyl chloride, and fusing off when it had been in the vapour for 10 minutes. When cool, it was opened under water, and the volume of residual air determined; from this and the total capacity of the bulb the temperature was easily calculated. Three temperatures determined in one day only varied by 7°; the numbers found were 690·6°, 692·3°, and 697·8°.

Four determinations of the density were conducted in the sulphur vapour. In the first two, we liquefied the gas in the bulb, and allowed all excess to boil away after the neck had been drawn out into a long capillary. At first, we experienced great difficulty in keeping the bulbs free from moisture whilst the gas was passing in; we eventually got over this difficulty by fixing a long T-tube on to the neck of the bulb, and leading the gas through a capillary which passed down the T-tube, and reached to the bottom of the bulb, where it was condensed. In the last two experiments conducted at this temperature, we merely passed the gas through the bulbs for about 30 minutes. The four results agreed fairly well, ranging from 32·3 to 33·1, and thus they indicate that no dissociation had taken place.

Air-bath.

We next made two determinations of the density in an air-bath, which was heated by means of four large Bunsen burners. The temperature was determined both before and after each experiment by means of air thermometers. The bulbs were filled with the chloride by passing the gas through, and the two following results were obtained:—

Temperature......	796°	V. d.	31·36
Temperature......	816°	V. d.	31·00

These numbers indicate a percentage decomposition of about 13.

Combustion Furnace.

Our last experiments were conducted in a combustion furnace. We first used a method similar to that adopted by V. Meyer and Züblin in their investigations on chlorine, oxygen, &c., at high temperatures (*Berichte*, 12, 1430). The tube used was an ordinary piece of combustion tubing, the same length as the furnace; to one end was fixed a tap, whilst the other was drawn off into a capillary.

A determination of the temperature was made both before and after each experiment.

The tube was first dried by aspirating dry air through it for half an hour whilst the tube was red hot. The tap was then turned off and the tube allowed to remain at the temperature of the furnace for 10 minutes; the residual air was then measured by driving it into a Schiff's nitrometer, filled with strong caustic potash solution. A stream of carbon dioxide, dried by passing through two sulphuric acid tubes, was used for driving the air over.

The carbon dioxide, in its turn, was displaced by the nitrosyl chloride, which was allowed to pass through the tube for about half an hour. A flask was attached to the capillary at the end of the tube in order to prevent diffusion. That a certain amount of dissociation did take place was proved by the fact that the gas which passed out of the flask turned red on meeting the air, thus showing the presence of a certain amount of nitric oxide. When we considered that all the carbon dioxide had been displaced, the tap was again turned off and the tube allowed to remain for 10 minutes. The nitrosyl chloride was then driven out by means of a stream of carbon dioxide into a Varrentrap's bulb, containing either distilled water or ammonia. When all had been absorbed, the solution was treated as in the former experiments, and the chlorine estimated. Another determination of the temperature was then made by aspirating dry air through the tube, allowing it to expand, and measuring the residue in the nitrometer. We found that the temperatures were generally very concordant, rarely differing by more than 10°, and often coming within 1 or 2 degrees of each other. Three determinations of the vapour density were made in this way with the furnace at its full heat. The results obtained were 29·73, 29·1, and 29·1. In all these cases we found that the nitrosyl chloride acted on the glass tube forming chlorides of the alkalis. These were volatilised by the great heat, and deposited in the capillary. As the gas was kept passing through the tube for some time, the amount of these chlorides was quite appreciable.

We, therefore, made several determinations in the combustion furnace, the gas having previously been liquefied in the tube. This we accomplished by taking a piece of combustion tubing nearly the same length as the furnace, rounding off one end, and drawing the other out slightly. Three or four cubic centimetres of the chloride were then condensed in the tube, and whilst it was still in the freezing mixture the open end of the tube was drawn out into a very fine capillary; the excess of nitrosyl chloride was allowed to boil away, then the tube was warmed by placing it on the bricks over the furnace. A small bulb was fixed on to the capillary to serve as a reservoir, and thus prevent diffusion. When warm, the tube was pushed straight into the hot furnace, the bed of which was lined with asbestos paper in order to keep the tube from sticking, and also to facilitate the pulling in and out of the tube. The tube was left in the furnace for about a quarter of an hour; the capillary was then sealed off and the tube pulled out. When cool, the end was broken off under water, and from the solution thus obtained the density was calculated by estimating the chlorine in the usual way. The temperature was determined both before and after each experiment by means of air thermometers. These consisted of tubes approximately of the same length as that used for the nitrosyl chloride. They were first thoroughly dried, then pushed into the hot furnace, left for 10 minutes, sealed off, pulled out of the furnace, and, when cool, opened under water.

An experiment conducted in this way, with the burners only partly on, gave a mean temperature of 784°, and a density of 31·77. Another experiment at 928° gave a result of 29·0.

Two more experiments gave the following:—

Mean temperature....	968°	V. d.	27·3
*Mean temperature....	985°	V. d.	27·0

This indicates a dissociation of practically 50 per cent. of the nitrosyl chloride molecules at a temperature not much below 1000°.

As we were not able to obtain higher temperatures with the apparatus at our command, and using glass tubes, we concluded our experiments at this stage.

The table (p. 80) gives a *résumé* of the results of our experiments.

From these results, it is evident that nitrosyl chloride behaves in a very different manner from nitrogen dioxide when subjected to high temperatures. Thus, at 620°, a temperature at which nitrogen dioxide is completely dissociated, nitrosyl chloride shows not the least trace of dissociation; and near 1000°, only about 50 per cent. of the molecules are dissociated. This fact would seem to point to a difference in the constitution of the molecules of the chloride and the oxide of nitrosyl, as nitrogen dioxide may be called.

Nitrosyl chloride, in its reactions with water, behaves as the chloride of nitrous acid, and inasmuch as nitrous acid not only forms nitroso-compounds, but by acting on the group $=CH_2$ produces oximes, $=C:N\cdot OH$, nitrous acid would appear to have the formula

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* The following are a few of the results with the air tubes; they show that the estimations of temperature were fairly concordant, and may be relied upon:—

(1.) 925·2°	(1.) 967°
(2) 930·0°	(2.) 969°

Vapour Density of Nitrosyl Chloride between 15° *and* 985°.

Method adopted for obtaining bulb full of gas.	Bath.	Temperature.	V d. (H = 1)	Per cent. amount of dissociation.
Passing gas for 45 mins ..	Air...	15°	32·57	0
Liquefying.............	Sulphuric acid	15	32·50	0
"	"	65	33 04	0
"	"	115	32·50	0
"	"	165	32·18	0
Passing gas.............	Methyl salicylate ...	222	32·30	0
"	Sulphur vapour....	693	32·90	0
"	"	693	32·31	0
Liquefying	"	693	33·24	0
"	"	693	33·12	0
"	Combustion furnace	784	31·77	8·09
Passing gas.............	Air-bath	796	31·36	11·86
"	"	815	31·00	15·17
Liquefying	Combustion furnace	928	29·00	33·51
Passing gas.............	"	964	29·73 ?	
"	"	965	29·10 ?	
"	"	965	29·10 ?	
Liquefying	"	968	27·30	49·21
"	"	985	27·00	51·97

V. d. calculated for NOCl .... 32 65.
V. d. calculated for complete dissociation .... 21·78.

O⁚N·OH, and the chloride therefore O⁚N·Cl. Now, NOCl is incapable of directly combining with oxygen, and the compound NO_2Cl seems to have no existence (Williams, Trans., 1886, 49). Hence, we must suppose that that part of the valency of nitrogen which in NO is concerned with linking on another atom of oxygen to form NO_2 or N_2O_4 (according to temperature) is already occupied by chlorine in NOCl.

Since nitric oxide, NO, and nitrosyl chloride, NOCl, show no tendency to polymerise, the union which is established between NO_2 and NO_2 at temperatures below 140° is probably owing to the oxygen. We have been accustomed to regard nitric peroxide as nitroso-nitric anhydride, representing it by the formula $O{:}N{\cdot}O{\cdot}N{<}^{O}_{O}$, but since the molecules of NO_2, concerned in the process of combination, are all alike, an unsymmetrical formula seems improbable.

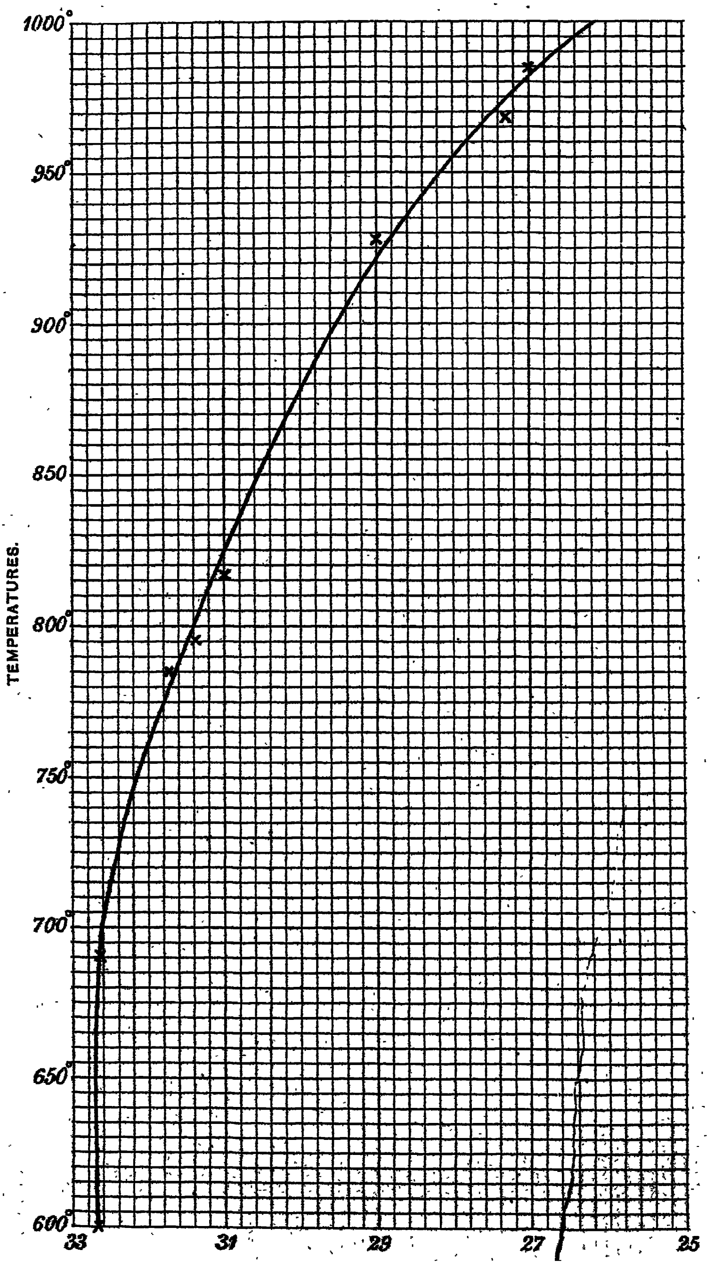
The formula O⁚N·O·O·N⁚O seems to satisfy the requirements of the case, as it would account for the formation of nitric, as well as of nitrous, acid by the action of water,

$$\begin{array}{c} O{:}N{\cdot}O\text{—}\text{—}O{\cdot}N{:}O \\ H \quad HO \end{array}$$

SUDBOROUGH

Journ. Chem. Soc. Feb. 1891.

CURVE SHOWING VAPOUR DENSITY OF NITROSYL CHLORIDE BETWEEN 600° AND 1000° C.



and this leads to the formula O:N·O– for the dioxide. This may, perhaps, account for the instability of this oxide at high temperatures by representing it as due to the unsaturated condition of the oxygen, while the more stable chloride may owe its greater permanence at high temperatures to the fact that the chlorine is not in the same degree unsaturated.

In conclusion, we have to thank Dr. Tilden for suggesting the work and supervising most of the experiments.

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Birmingham.

XI.—*The Fermentation of Calcium Glycerate by the "Bacillus Ethaceticus."*

By Percy F. Frankland, Ph.D., B.Sc. (Lond.), F.I.C., Professor of Chemistry in University College, Dundee; St. Andrews University; and William Frew, F.C.S.

In a communication to the Royal Society by one of us, "On a Pure Fermentation of Mannite and Glycerin," by P. F. Frankland and J. Fox (*Proc. Roy. Soc.*, **46**, 345), a micro-organism was described, having the power of fermenting suitable solutions of mannite and glycerin, and, in consequence of ethyl alcohol and acetic acid being the principal products of these fermentations, the name of *B. ethaceticus* was proposed for the organism in question.

In this paper, it was pointed out that the bacillus was also capable of setting up fermentative decompositions of glucose, cane-sugar, milk-sugar, starch, and calcium glycerate, but, most curiously, not of dulcite, although isomeric with and so closely akin to mannite.

The present paper deals with the fermentation of calcium glycerate by this organism.

Character of the Fermentation of Calcium Glycerate.—If sterile solutions (3 per cent.) of calcium glycerate to which the necessary nutritive material (see below), in the shape of a small quantity of peptone and minerals salts, has been added, are inoculated with a pure growth of the bacillus and kept at 35—38°, the liquid becomes turbid in the course of two or three days, and a day or two later a gentle but visible evolution of gas commences and continues for a period of about 7—14 days, after which the liquid again gradually becomes clear, although of considerably darker colour than at first. Occasionally, however, a feeble secondary fermentation may follow the cessation of the first and continue for a few days.

The fermentation of calcium glycerate, as measured by the visible evolution of gas, is very much less vigorous than the fermentations previously described, and the organism not unfrequently entirely loses its capacity of setting up a palpable fermentation in this medium; we have, however, generally been able to restore its fermentative power by inoculating into the calcium glycerate solution from a vigorously fermenting solution of mannite or glucose. The restoration of its fermenting power towards calcium glycerate is, however, sometimes exceedingly troublesome.

All the precautions mentioned in the previous paper were taken both as to the use of perfectly pure cultures of the bacillus and as to the prevention of contamination during the process of fermentation, whilst the purity of the solutions was similarly tested by cultivation before proceeding to the chemical examination of the products formed.

The purity of the calcium glycerate employed was tested by determination of the calcium in the air-dried substance:—

0·2923 gram of the substance yielded 0·1365 gram $CaSO_4$, corresponding to 13·73 per cent. Ca; calcium calculated upon $(C_3H_5O_4)_2Ca + 2H_2O$ gives 13·98 per cent.

The water of crystallisation is only partially lost at a temperature of 105—110°; thus the salt, on drying at that temperature, lost only 5·61 per cent., whilst the loss corresponding to 1 mol. H_2O is 6·29 per cent.

Fermentation No. 1.—The solution for fermentation had the following composition:—

Calcium glycerate........	60 grams	the whole diluted to 2000 c.c. with distilled water.
Peptone	2 "	
Calcium carbonate........	10 "	
Salt solution*............	200 c.c.	

The liquid was contained in a large flask plugged with cotton wool, and, after due sterilisation, was inoculated with a needle-loop of a pure culture of the *Bacillus ethaceticus*, and then kept in an incubator at 38°. Fermentation began on the 3rd, and was practically finished on the 7th day; the flask was not, however, removed from the incubator and examined until the 26th day.

The liquid was then submitted to distillation until a small quantity of the distillate yielded only the faintest reaction with Lieben's test (iodoform). The distillate, in which alcohols were to be expected, was found to be free from aldehyde, as indicated by the absence of reaction with rosaniline.

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* Prepared by dissolving 1 gram of potassium phosphate, 0·2 gram of magnesium sulphate (cryst), and 0·1 gram of calcium chloride (fused) in 1000 c.c. of distilled water.

The alcohols in the liquid were determined by oxidation with potassium dichromate and sulphuric acid (A. Dupré, *J. Chem. Soc*, **20**, 495). For this purpose 10 grams of potassium dichromate and 20 grams of strong sulphuric acid were made up to 100 c.c. with water, and 10 c.c. of this solution were added to every 20 c.c. of the alcoholic solution; the chromic acid solution, along with the alcoholic liquid, was placed in bottles, the mouths of which were closed with india-rubber stoppers tightly wired down. The bottles were then heated for seven hours in a steamer at 100°. The chromic acid was then reduced by the addition of a calculated quantity of zinc, and after the latter had passed into solution, the liquid was repeatedly distilled down to a small bulk, fresh quantities of water being added each time. In this manner, any volatile acids produced in the previous oxidation were obtained in the distillate. These acids were converted into barium salts by treatment with barium carbonate. The barium salts were dried at 130°, and the barium determined by conversion into barium sulphate. The following quantities of barium salts were obtained:—

I. 1·3915 gram barium salt, yielding 91·16 per cent. $BaSO_4$ (barium acetate yields 91·37 per cent. $BaSO_4$).

II. 1·9470 gram barium salt, yielding 91·16 per cent. $BaSO_4$.

III. 1·4010 gram barium salt, yielding 91·40 per cent. $BaSO_4$.

The barium salts were thus practically pure barium acetate, indicating that the liquid before oxidation contained ethyl alcohol, and inasmuch as 4·7395 grams of barium acetate were in all obtained, ethyl alcohol to the extent of 1·711 gram must have been present.

In order to test this method of determining alcohol by oxidation, we have made experiments with known quantities of pure alcohol; the results of these determinations are recorded in the Appendix (see p. 93).

The residue from the first distillation of the fermented liquid was now treated with the requisite quantity of standard hydrochloric acid to neutralise the total calcium (both as glycerate and carbonate) present. 22·61 grams of HCl (or 619·4 c.c. of normal hydrochloric acid) were required for this purpose, but only 350 c.c. were in the first instance added, and then the liquid was repeatedly distilled to a small bulk in order to get over the volatile acids; the latter were converted into barium salts and analysed as above:—

I. 10·5940 grams barium salts, yielding $BaSO_4 \begin{cases} 91·69 \text{ per cent.} \\ 91·88 \quad ,, \end{cases}$

100 c.c. more of the normal hydrochloric acid were added to the flask and distillation continued, from which the following salts were obtained:—

II. 4·1505 grams barium salts, yielding $BaSO_4 \begin{cases} 96·50 \text{ per cent.} \\ 96 34 \quad ,, \end{cases}$

After a further addition of 100 c.c. normal HCl, there were obtained:—

III. 0·5685 gram barium salts, yielding $BaSO_4$ 90·00 per cent. (the salt was pasty in appearance).

The remainder (69·4 c.c.) of the normal hydrochloric acid was then added, after which there were obtained:—

IV. 0·209 gram barium salts, yielding 84·68 per cent. $BaSO_4$ (the salt was again pasty in appearance).

10 c.c. of normal hydrochloric acid over and above the calculated amount were then added, but no further volatile acids could be obtained in the distillate.

In this and in similar experiments, we have always found that the last quantities of volatile acid obtained by repeated distillation in this manner are pasty and yield a low percentage of barium; we are, therefore, of opinion that the low percentages of barium in the fractions III and IV do not indicate the presence of volatile fatty acids of higher molecular weight, especially as such acids if they had been present should have come over in the first fraction (see Appendix, p. 95).

The salts thus consist of a mixture of barium acetate and formate, and taking into account that

Barium acetate yields 91·37 per cent. $BaSO_4$,
,, formate ,, 102·64 ,, ,,

it can be calculated that the above salts consisted of 12·8873 grams barium acetate (or acetic acid, 6·065 grams) and 2·6347 grams barium formate (or formic acid, 1·067 gram), equivalent to 1·391 gram acetic acid.

In the liquid from which the volatile acids had been distilled off as above, there was left a brown, flocculent deposit; this was filtered off and washed with dilute hydrochloric acid. It was found to be entirely soluble in a boiling solution of caustic potash, from which it was again precipitated by hydrochloric acid. After thoroughly washing and drying until constant at 100°, it was found to weigh

0·0845 gram. This substance is of constant occurrence in all the fermentations with which we are acquainted, and appears to be derived from the cells of the bacteria themselves. It is the only portion of the fermentation products insoluble in dilute hydrochloric acid. Owing to the small quantity in which it is produced, however, we are not in a position to offer any further information as to its nature.

The filtrate from the above insoluble residue would obviously contain any unaltered calcium glycerate, together with any fixed acid that might have been produced in the fermentation; such acids would, however, be in the free state, inasmuch as an excess of hydrochloric acid had been added to the liquid. The liquid was repeatedly shaken out with ether. The ethereal extract, on drying at 100°, only amounted to 0 4785 gram, and a considerable part of this appeared to be succinic acid mixed with some gummy material.

The liquid, after extraction with ether as above, was boiled up with excess of calcium carbonate and filtered; the filtrate was evaporated to dryness on a water-bath, and then extracted with a large quantity of strong methylated spirit (93 per cent.), in order to separate any unaltered calcium glycerate. (We had previously determined that calcium glycerate can be most perfectly precipitated from solution by addition of strong spirit.) The calcium salt thus separated was unfortunately not weighed itself, but was converted into a lead salt by precipitation with lead acetate and alcohol. The lead salt thus obtained, after recrystallisation from water, yielded 68·89 per cent. of lead, corresponding closely to one of the basic lead glycerates referred to below (see pp. 87, 90).

After removing the calcium glycerate precipitated by means of alcohol as above, the alcoholic filtrate was evaporated down until free from alcohol, the residue was taken up with water, and the calcium precipitated with very slight excess of sodium carbonate, after which the calcium carbonate was filtered off. The filtrate, containing the sodium salts, was evaporated to dryness and repeatedly extracted with a mixture of 3 parts ether and 1 part alcohol, as it was thought that possibly some glycerin might have been formed in the fermentation; none was however found. The residue was then dried at 100—105° and weighed; it amounted to 71·408 grams. In addition to sodium chloride, this residue evidently contained the sodium salt of an organic acid, as it charred on heating. It was found to contain 82·02 per cent. of ash, and 68·28 per cent. of sodium chloride, leaving thus a considerable margin for the sodium salt of the organic acid. From this mixture, the sodium was as far as possible removed as sodium chloride by saturating the solution with hydrochloric acid gas. After filtering off the sodium chloride and washing with strong hydrochloric acid, the filtrate was evaporated to dryness and dried at 100°. The organic acid thus obtained (containing of course a small quantity of sodium chloride also) amounted to 15·790 grams; of this 13·400 grams were soluble in alcohol, 1·733 gram insoluble in alcohol but soluble in water, and 0·657 gram insoluble both in alcohol and water. The organic acid itself may thus be taken to have amounted to about 13·4 grams, whilst the remainder would be principally sodium chloride.

Some of the acid thus obtained was converted into a barium salt by boiling up with barium carbonate and filtering; the filtrate was evaporated to dryness and the residue dissolved in a small quantity of water, and treated with a large excess of alcohol, which produced a gummy precipitation. This precipitate was washed with alcohol several times, and then divided into several different portions, which were dried at different temperatures, and a barium determination made in each, thus:—

No. 1 dried at 105° yielded $BaSO_4$	62·76 62·82	per cent. ,,
No. 2 dried at 110—120° yielded $BaSO_4$	64·08	,,
No. 3 dried at 130° yielded $BaSO_4$....	64·95	,,
No. 4 dried at 140° ,, ...	65·53	,,

In a specimen of pure barium glycerate, after drying at 140°, we found the yield of barium sulphate to be 66·59 per cent. Even when dried at this temperature, the salt is not anhydrous, as anhydrous barium glycerate should yield 67·14 per cent. of barium sulphate. The effect of drying at different temperatures on pure barium glycerate was specially determined with the following results:—

Barium glycerate dried at	100—105°	yielded	65·51	p.c. $BaSO_4$.
,, ,,	130°	yielded	66·55	p.c. $BaSO_4$.
,, ,,	140°	,,	66·59	,, ,,

The coincidence between the barium salt in question and barium glycerate is thus very marked, for the percentage of barium itself in the latter is 39·16, and in the former 38·53.

We next endeavoured to obtain a lead salt of the acid by boiling its aqueous solution with lead carbonate and filtering; on cooling, a deposition took place in the filtrate; this precipitate was washed, dried, and submitted to analysis with the following results:—

A lead determination made on the salt dried over sulphuric acid, yielded 66·97 per cent. lead.

Another made on the salt dried at 100—105° yielded 66·99 per cent. lead.

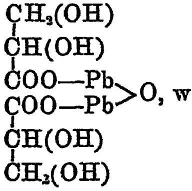
In spite of repeated recrystallisation, we failed to obtain the lead salt free from chlorine, and it became necessary, therefore, to determine the latter; by precipitation with silver nitrate, 1·95 per cent. of chlorine was obtained.

0·5065 gram of the salt dried at 105° yielded, on combustion with CuO and a silver roll placed in front, 0·05275 gram OH_2, and 0·1865 gram CO_2.

The two following percentage compositions can be calculated from these results, according as we assume that the chlorine is present as $PbCl_2$ or as Pb_2OCl_2:—

	(*a.*) Calculating Cl as $PbCl_2$.	(*b.*) Calculating Cl as Pb_2OCl_2.
Pb	66·54	64·52
C	10·87	11·64
H	1·25	1·34
O	21·34	22·50
	100·00	100·00

The percentage composition (*b*) is in very fair accord with that of a basic salt of the formula—



$$\begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ COO{-}Pb \\ \qquad\qquad > O \\ COO{-}Pb \\ | \\ CH(OH) \\ | \\ CH_2(OH) \end{array}$$

, which requires

Pb	64·68
C	11·25
H	1·56
O	22·51
	100·00

Fermentation No. 2.—The conditions of this experiment were precisely similar to those in the Fermentation No. 1.

The examination of the fermentation products was made upon essentially similar lines to those laid down above. Unfortunately, however, the liquid containing the alcohols was lost during the process of oxidation with chromic acid, through the bursting of the closed bottle in steaming. The absence of aldehyde was, however, again confirmed.

The volatile acids were dealt with as before, and the following barium salts prepared and analysed:—

I. 11·684 grams barium salt, yielding $BaSO_4$ $\begin{cases} 91·64 \text{ per cent.} \\ 91·73 \quad " \end{cases}$

Corresponding to 11·364 grams barium acetate and
0·320 " " formate.

II. 3·4465 grams barium salt, yielding $BaSO_4 \begin{cases} 97·40 \text{ per cent.} \\ 97·56 \quad ,, \end{cases}$

Corresponding to 1·578 gram barium acetate and
1·8685 ,, ,, formate.

III. 0·4995 gram barium salt, of pasty appearance, which, after extraction with strong alcohol, left 0·3215 gram insoluble; this yielded 97·35 per cent. $BaSO_4$,

Corresponding to 0·147 gram barium acetate and
0·174 ,, ,, formate.

IV. 0·1255 gram barium salt, again of very pasty appearance, but as the quantity was too small to purify as above, it was converted into $BaSO_4$, of which it yielded only 82·47 per cent.; assuming, however, that it had the same proportional composition as fraction III, it would correspond to 0·0575 gram barium acetate, and 0·068 gram barium formate.

Thus the total yield of volatile acids consisted of:—

13·1465 grams barium acetate, corresponding to 6·187 grams acetic acid,

2·4305 grams barium formate, corresponding to 0·985 gram formic acid.

After distilling off the volatile acids, there remained, as in the case of the first fermentation, a brown, insoluble residue which, after thoroughly washing free from hydrochloric acid and drying at 105°, amounted to 0·1665 gram.

From the filtrate, there was obtained by repeatedly shaking out with ether an extract which, after drying at 100°, amounted to 0·501 gram, and appeared to consist to a great extent of succinic acid mixed with some gummy material, just as in the previous fermentation.

The acid liquid, after extracting with ether as above, was boiled up with an excess of calcium carbonate, filtered, and the filtrate evaporated as nearly to dryness as possible on the water-bath. The residue of calcium salts was then extracted with a large quantity of strong alcohol (93 per cent.), and further quantities of alcohol were added to the liquid until no more precipitation was occasioned. The insoluble part, consisting presumably of unaltered calcium glycerate, was filtered off; it was quite soluble in water, and amounted, after drying at 105°, to 2·037 grams (corresponding to 1·61 grams of glyceric acid, taking into account the loss of a part of the water of crystallisation at 105°, see p. 82). This calcium salt was purified by dissolving in water and precipitating with alcohol four times, after which it was dried at 105—110°, and a calcium determination made, which yielded 14·29 per cent. of calcium. Pure calcium glycerate, when similarly dried, was found to yield 14·81 per cent. of calcium.

After removal of the above calcium glycerate, the further treatment was similar to that described for the first fermentation; in the first instance, the calcium was precipitated by means of a very slight excess of sodium carbonate, the sodium was then removed as far as possible by saturating with hydrochloric acid gas, and filtering off the precipitated sodium chloride. On evaporating the filtrate to dryness on the water-bath and drying at 100°, there remained 18·11 grams of residue (consisting of an organic acid, with a little sodium chloride which had escaped precipitation); of this, 13·90 grams were soluble in alcohol (90 per cent.), 2·81 grams were insoluble in alcohol, but soluble in water, therefore doubtless sodium chloride, whilst 1·40 gram was insoluble in water also. The amount of organic acid, 13 90 grams, was thus almost identical with that obtained in the previous fermentation, 13·40 grams.

Owing to the unsatisfactory and gummy appearance of the barium salt prepared from this organic acid in the first fermentation, we determined on this occasion to prepare only the lead salt. For this purpose, the portion of the above residue soluble in alcohol was dissolved in water, boiled up with lead carbonate, and filtered hot; on cooling, however, no deposition of lead salt took place. We therefore decomposed the solution with sulphuretted hydrogen, filtered off the lead sulphide, heated the filtrate until free from sulphuretted hydrogen, and then again boiled up with lead carbonate and filtered. On cooling, a quantity of lead salt separated from the filtrate; this we washed, dried at 105°, and submitted to analysis:—

$$\text{The salt yielded Pb} \ldots\ldots\ldots\ldots\ldots\ldots \begin{cases} 68\cdot66 \text{ per cent.} \\ 68\cdot69 \quad ,, \end{cases}$$

As this lead salt was also found to contain chlorine, as in the case of the one obtained in the first fermentation, a determination of the halogen was made by precipitation with silver nitrate, with the following result:—

$$\text{Chlorine} \ldots\ldots\ldots\ldots\ldots\ldots \begin{cases} 1\cdot13 \text{ per cent.} \\ 1\cdot23 \quad ,, \end{cases}$$

On combustion in oxygen with CuO and silver foil in front, the following results were obtained:—

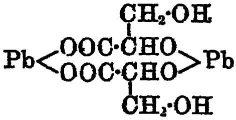
I. 0·5525 gram yielded 0·060 gram OH_2, and 0·203 gram CO_2; corresponding to H = 1·21 per cent., C = 10·02 per cent.

II. 0·59525 gram yielded 0·065 gram OH_2, and 0·21675 gram CO_2; corresponding to H = 1·21 per cent., C = 9·93 per cent.

Assuming, however, that the chlorine found in the salt is present as $PbCl_2$ or as Pb_2OCl_2. the following figures may be calculated respectively:—

	Cl as $PbCl_2$.	Cl as Pb_2OCl_2.
Pb..........	68·39	67·47
C..........	10·48	10·79
H..........	1·26	1·32
O..........	19·87	20·42
	100 00	100 00

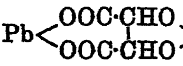
On comparing these with the results obtained in the case of the similar salt in the first fermentation, it will be seen that this one contains more lead in proportion to the carbon and hydrogen, which is doubtless due to its being a more basic salt, or possibly a mixture of the former salt with a more basic one. This becomes the more probable when it is remembered that this salt was only precipitated after *repeatedly* boiling with lead carbonate, and that after each successive treatment with lead carbonate, a fresh quantity of precipitate formed on cooling. In fact, this second lead salt corresponds approximately in composition with a basic salt of the following constitution:—



$$\mathrm{Pb}\left<\begin{array}{l}\mathrm{CH_2\cdot OH}\\ \mid\\ \mathrm{OOC\cdot CHO}\\ \mathrm{OOC\cdot CHO}\\ \mid\\ \mathrm{CH_2\cdot OH}\end{array}\right>\mathrm{Pb}$$

Pb........	66·56
C.........	11·57
H.........	1·28
O.........	20·59
	100·00

A similar basic salt has been prepared in the case of tartaric acid, and has the formula

 (Erdmann, *Annalen*, 21, 14).

$$\mathrm{Pb}\left<\begin{array}{l}\mathrm{OOC\cdot CHO}\\ \mid\\ \mathrm{OOC\cdot CHO}\end{array}\right>\mathrm{Pb}$$

Unfortunately, the quantity of material at our disposal was insufficient to effect any further purification of the salt, and we have had to leave the further investigation of this acid until a larger quantity of the products of fermentation have been obtained. It is, however, perfectly obvious that this non-volatile acid left after fermentation has the very strongest resemblance, both in composition and properties, to glyceric acid, and we hope very shortly to be in a position to communicate some further points of interest and importance concerning it.

Fermentations Nos. 3 *and* 4.—Two further fermentations were conducted in order to re-determine the quantities of alcohol and volatile acids produced, as well as the relationship between the two. The mode of procedure was just the same as before, and the following quantities of products were obtained on aliquot parts of the whole fermented liquid:—

Volatile Acids.

	Fermentation III.	Fermentation IV.
Barium salt dried at 130°.	2·015 grams, yielding $BaSO_4$ 91·96 per cent.	3·813 grams, yielding $BaSO_4$ 92·10 per cent.
Total barium salt produced	(2·015 × 4 = 8·06 grams). See note below	3·813 × 4 = 15·252 grams
Corresponding to—		
Acetic acid	(3·694 grams)	7·00 grams
Formic "	(0·0806 ")	0·132 "
Total volatile acid, calculated as acetic acid	(3·799 ")	7·198 "

Alcohols on Oxidation yielded:—

Barium salt dried at 130°.	1·3125 gram, yielding $BaSO_4$ 90·95 per cent.	1·8015 gram, yielding $BaSO_4$ 90·95 per cent.
Total barium salt produced	(1·3125 × $\frac{3}{2}$ = 1·968 gram)	1·8015 × 2 = 3·603 grams
Corresponding to ethyl alcohol	(0·71 gram)	1·299 gram

Note.—Only in the case of No. IV are the quantities of alcohol and acetic acid obtained absolute, for in No. III about one-half of the fermented liquid was accidently lost just in commencing the first distillation. Thus, whilst the proportion of alcohol to acetic acid remained undisturbed by the mishap, the amounts of alcohol and acid must be multiplied by about 2, in order to obtain the quantities actually produced in the fermentation

From these results, the alcohol and acetic acid are seen to stand in the following relationship:—

Fermentation III. Alcohol : acetic acid :: 1 : 5·35
" IV. " " :: 1 : 5·54

This relationship corresponds approximately to 1 mol. of alcohol to 4 mols. of acetic acid:—

$$C_2H_5{\cdot}OH : 4(CH_3{\cdot}COOH) = 46 : 240 = 1 : 5{\cdot}2.$$

Of Fermentations Nos. 1 and 2, only No. 1 can be used for comparison, as in No. 2 the portion containing the alcohol was lost. In No. 1 the relationship was,

Alcohol : acetic acid :: 1 : 4·35.

We believe that this deficiency of acetic acid in the case of No. 1 is probably to be accounted for by the very considerable proportion of formic acid produced in that fermentation, for there is evidence, as already pointed out by one of us in the case of mannite and glycerin, that whenever formic acid is found amongst the products of fermentation of the *Bacillus ethaceticus*, the proportion of acetic acid is diminished, and we are of opinion that the formic acid is produced at the expense of the acetic acid already formed, in that feeble secondary fermentation, mentioned on p. 82, which occasionally takes place. This belief is supported by the fact that in the case of Nos. 1 and 2, in which the amount of formic acid was considerable, such a secondary fermentation was actually observed, whilst in the case of Nos. 3 and 4, in which the proportion of formic acid was quite insignificant, it was not.

We may provisionally suggest the following as the equation according to which the glyceric acid undergoes fermentative decomposition by this organism:—

$$5C_3H_6O_4 = C_2H_6O + 4C_2H_4O_2 + OH_2 + 5CO_2 + 3H_2.$$

This equation not only indicates the observed relationship between the alcohol and acetic acid formed, but the proportion of these substances to the glyceric acid decomposed is in fair accord with the quantities actually obtained. Thus, in Fermentations 1 and 2, there were in each case 60 grams of calcium glycerate, corresponding to 44·47 grams of glyceric acid, employed, and of this, almost exactly one-half was still present as glyceric acid after the fermentation was completed; assuming, then, that 22 grams of glyceric acid had suffered fermentative decomposition, there should have been formed, according to the above equation, 1·9 gram of alcohol and 9·9 grams of acetic acid; as a matter of fact, there were actually found by the methods of analysis employed, 1·7 gram alcohol in Fermentation 1 (in Fermentation 2 the alcohol was lost), and 1·3 gram alcohol in Fermentation 4, also 7·5 grams volatile acid calculated as acetic acid in Fermentation 1, 7·47 grams in Fermentation 2, and 7·2 grams in Fermentation 4. Now, it will be shown in the Appendix to this paper (see pp. 94, 95) that, in the process of repeated distillation with hydrochloric acid, only about 95 per cent. of the volatile acid present is actually recovered, so that, by introducing this correction, the above figures approximate more closely to those calculated from the equation, and the difference may doubtless be accounted for by loss in the secondary change from acetic to formic acid, as well as in the production of the small quantity of succinic acid, which has not been taken into consideration in the equation.

We may summarise the results of our investigation as follows:—

(1.) Suitable solutions of calcium glycerate undergo a very well-defined fermentation on inoculation with pure cultures of the *Bacillus ethaceticus.*

(2.) The fermentation is less vigorous than those induced by the same organism in similar solutions of glucose, mannite, and glycerin; indeed, in old cultures the organism is frequently found to have lost its power of fermenting the glycerate, although it still grows in the solution, rendering it highly turbid.

(3.) The products of the fermentation are essentially alcohol and acetic acid, with a small and variable proportion of formic acid, together with a trace of succinic acid.

(4.) The alcohol and acetic acid are produced approximately in the proportion of 1 mol. of alcohol to 4 mols. of acetic acid.

(5.) The production of formic acid appears to be at the expense of acetic acid, as previously observed by one of us in the case of other fermentations induced by this organism.

(6.) There remains, after the completion of the fermentation, in addition to the above products, also the calcium salt of a fixed acid, the amount of which corresponds almost exactly to one-half of the glyceric acid originally present. We have reason to believe that this acid is glyceric acid, but we are still engaged upon its further investigation.

APPENDIX.

We wish to record in this appendix some of the experiments undertaken with a view to testing the accuracy of the methods employed in the separation of the various products of the fermentation.

I. *Determination of Alcohol by Oxidation with Potassium Dichromate and Sulphuric Acid.*

10·7475 grams of absolute alcohol (calculated from sp. gr. of strong spirit of wine) were diluted to 1000 c.c. with distilled water; 100 grams of potassium dichromate and 200 grams of strong sulphuric acid dissolved in 1000 c.c. of water were then added, and the whole was heated in a closed bottle at 100° for seven hours. The liquid was then reduced with zinc, the total volume now amounting to 2070 c.c. Of this, 255 c.c. (containing the products of oxidation of 1·323 gram alcohol corresponding to 1·727 gram acetic acid) were taken and submitted to repeated distillation as long as the distillate came over acid; on titrating the three distillates so obtained with normal alkali, the following quantities of acid, calculated as acetic acid, were recovered:—

Distillate.	Acidity, calculated as acetic acid.
I	0·762 gram
II	0·929 „
III	0·004 „
Total......	1·695 „

1·695 gram acetic acid corresponds to 1·299 gram ethyl alcohol, so that 98·17 per cent. of the alcohol employed was actually found.

II. *Determination of the Volatile Acids by Distillation with Hydrochloric Acid.*

In the first experiment:—

5 grams of pure barium formate were dissolved in about 200 c.c. of water and a quantity of (20 c.c. of normal hydrochloric acid) hydrochloric acid insufficient to decompose the whole of the formate was added; the liquid was then repeatedly distilled to one quarter of its bulk until the distillate was no longer acid. Each distillate was then titrated with normal alkali, and the following quantities of formic acid were thus obtained in the several distillates:—

Distillate.	Acidity, calculated as formic acid.
I	0·4784 gram
II	0·2300 „
III	0·0920 „
IV	0·0460 „
V	0·0090 „
VI	0·0140 „
Total......	0·8694 „

This 0·8694 gram of formic acid actually found corresponds to 94·5 per cent. of the formic acid theoretically liberated by the quantity of normal hydrochloric acid originally added.

In a second experiment the conditions were varied:—

4·593 grams of barium formate were dissolved in about 750 c.c. of water, and then the calculated amount of normal hydrochloric acid was added so as to liberate the whole of the formic acid; the liquid was then repeatedly evaporated to about one-fourth of its bulk until the distillate was no longer acid, the various distillates were then titrated with decinormal alkali in quantities of 1000 c.c. at a time, when the following proportions of formic acid were found:—

Distillate.	Acidity, calculated as formic acid.
I	0·6900 gram
II	0·6440 „
III	0·2806 „
IV	0·0920 „
V	0·0506 „
VI	0·0115 „
Total....	1·7687 „

This total of 1·7687 gram corresponds to 95·00 per cent. of the formic acid which should have been theoretically found (namely, 1 862 gram).

III. *Determination of the Order of Distillation of the Fatty Acids.*

These experiments were made in order to ascertain the succession in which the several fatty acids distil over from a mixture of their salts to which hydrochloric acid has been added.

Thus a mixture of barium propionate, acetate, and formate was made in the proportion of:—

Barium propionate	3 000 grams
„ acetate	2·703 „
„ formate	2·406 „

Each of these quantities of salt requires 21·2 c.c. of normal hydrochloric acid for the liberation of its respective acid.

1. 21·2 c.c. of normal acid were added along with a considerable volume of water, and distillation was proceeded with as long as an acid distillate came over, fresh water being repeatedly added to the distilling flask. The acid in the distillate was then converted into barium salt in the usual way, and after drying at 130° until constant, the latter was weighed and a barium determination made:—

2·6825 grams of barium salt were obtained, yielding:—

(*a*.) 85·43 per cent. $BaSO_4$,
(*b*) 85·63 „ „

Barium propionate yields 82·13 per cent. $BaSO_4$.

2. The whole of the remaining acid (42·4 c.c. of normal hydrochloric acid) was then added, and distillation continued down to one-fourth the volume of liquid; from this first distillate, there were obtained:—

2·6515 grams barium salt, yielding $\begin{cases} 92{\cdot}42 \text{ per cent. } BaSO_4, \\ 92{\cdot}00 \quad ,, \quad ,, \end{cases}$

Barium acetate yields 91·37 per cent. $BaSO_4$,
,, formate ,, 102·64 ,, ,,

Water was again added, and the liquid distilled down to one-fourth of its volume; from this second distillate, there was obtained:—

1·549 gram of barium salt, yielding $\begin{cases} 96{\cdot}81 \text{ per cent. } BaSO_4. \\ 96{\cdot}65 \quad ,, \quad ,, \end{cases}$

This salt, therefore, contained a larger proportion of formate than the last.

The liquid was again three times distilled down to one-fourth of its bulk, and on uniting these distillates (3, 4, and 5), there was obtained:—

0·364 gram of barium salt, yielding 100·00 per cent. $BaSO_4$, and thus consisting chiefly of formate with a smaller proportion of acetate.

Two more distillates (the 6th and 7th) were similarly obtained and, on uniting them, a further quantity of—

0·2275 gram of barium salt was prepared, yielding 101·98 per cent. $BaSO_4$.

This was, therefore, almost pure formate.

These results clearly show, what has already been amply demonstrated in the course of our examinations of the fermented liquids, that from such a mixture of the salts of the fatty acids the acids distil over in the order of their molecular weights, the heaviest first and the lightest last.

XII.—*An Optically Active Glyceric Acid.*

By Percy F. Frankland, Ph.D., B.Sc. (Lond.), F.I.C., Professor of Chemistry in University College, Dundee; St. Andrews University; and William Frew, F.C.S.

Although it is upwards of ten years since the enunciation of Le Bel and Van't Hoff's theory concerning the optical activity of organic compounds, and although numerous discoveries of the highest importance have been made through the application of this theory, yet some of its fundamental demands still remain unsatisfied and ignored.

Prominent amongst the simple organic substances which, according to the theory, should be decomposable into two oppositely active optical isomers are lactic and glyceric acids, of which the former has, it is true, long been known in an active as well as an inactive form, although the active form has hitherto only been obtained as the result of vital agency, whilst glyceric acid is only known as a substance devoid of action upon polarised light.

In the preceding paper, we have described a fermentative decomposition of glyceric acid induced by a micro-organism previously isolated and described by one of us (*Proc. Roy. Soc.*, **46**, 345) as the *Bacillus ethaceticus*, in consequence of the products—alcohol and acetic acid—to which it gives rise in the fermentation of various substances. In this fermentation of glyceric acid, we were early struck by the remarkable fact that after the completion of the fermentation there remained a quantity (amounting to just about one half of the glyceric acid employed) of a fixed acid insoluble in ether and in other respects most closely resembling glyceric acid itself, although its purification, owing to its being mixed with a large quantity of calcium chloride, was invested with inordinate difficulties. We at once suspected that the fermentation had taken a similar course to that observed by Pasteur in his classical experiments on the decomposition of racemic acid, and which resulted in the destruction of the dextro- and in the persistence of the lævotartaric acid.

Special fermentations were, therefore, started with a view of ascertaining whether the fermented liquid was optically active or not.

Preliminary Experiments.

Three flasks were each furnished with the following ingredients :—

Calcium glycerate	15·0 grams	Diluted to 500 c.c. with distilled water.
Peptone................	0·5 „	
Salts, solution	50 c.c.	
Calcium carbonate	2·5 grams	

Two of these flasks were fermented with a pure culture of the *Bacillus ethaceticus* in the ordinary way, the third was preserved for control.

When the fermentation was completed, the contents of one of the fermented flasks and of the control flask were respectively filtered and evaporated down to a small bulk (100 c.c.) and examined with the polarimeter (a Mitscherlich "half-shadow" instrument). The unfermented liquid was found to be quite inactive, whilst the fermented one gave a rotation of —2°.

In order to obtain a more concentrated solution of the free acid, the calcium was precipitated by means of the calculated proportion of oxalic acid (after carefully determining the calcium in solution in the liquids from the fermented and control flasks respectively). The filtrate from the calcium oxalate was evaporated to a small bulk, boiled with animal charcoal, filtered, and again evaporated until the volume of the liquid was only 20 c.c. Some of this solution was examined with the polarimeter, and although it was too dark in colour for accurate observation in a 200 mm. tube, still an undoubted rotation of about −1° to −1·5° could be discerned.

On further making the volume up to 40 c.c. with distilled water, the rotation obtained was −0·5° to −0·75°. Exactly one-half of this liquid was carefully neutralised with sodium carbonate, and the volume made up to 25 c.c.; on examination in the same 200 mm. tube, it gave a rotation of −4° to −4·5°.

This rotation was very much more accurately measurable, as the liquid thus diluted was very nearly transparent.

The unfermented liquid was treated in exactly the same manner. The free acid made up to 20 c.c., on examination in the 200 mm. tube, was very dark coloured, and the readings were consequently very difficult to make, but a rotation of −0·75° was recorded, although probably due to experimental error, for when half of this was neutralised with sodium carbonate and made up to 25 c.c., the nearly transparent liquid yielded in the 200 mm. tube either no rotation at all or at most −0·5°, thus contrasting most markedly with that obtained in the case of the fermented liquid under precisely similar circumstances.

The contents of the second fermented flask, after filtration and reducing the volume by evaporation to 100 c.c., gave in the 200 mm. tube a rotation of −2°.

The calcium was again quantitatively removed by oxalic acid, the filtrate was twice boiled with animal charcoal, and the bulk then reduced to 20 c.c. by evaporation; on examination in a 200 mm. tube, the rotation at 18·5° was found to be −0·9°.

The half of this liquid was then neutralised with sodium carbonate, its volume made up to 25 c.c, and then examined in the 200 mm. tube at 17°; the rotation was −3·4°.

From these experiments, it was evident that the fermented liquid contained an active acid (apparently lævorotary), yielding a more active calcium and still more active sodium salt.

Experiments on a Larger Scale.

Two flasks, each containing 60 grams of calcium glycerate with the corresponding additions, were fermented in the ordinary way with a pure culture of the *Bacillus ethaceticus*. After completed fermentation, a portion was employed for the determination of the other products, whilst the remainder was taken for the special study of the residual acid. Of the volatile products, the alcohol was removed by evaporation, whilst the volatile and fixed acids were displaced by the addition of the calculated quantity of oxalic acid, and the volatile acids then dissipated by repeated evaporation on the water-bath. After filtering off the calcium oxalate, the liquid was repeatedly shaken out with ether to remove the fixed acids soluble in this medium. Only a very small quantity of impure succinic acid was thus extracted, as was to have been anticipated from our previous examinations of the fermentation products.

The liquid now containing only the residual acid was boiled with animal charcoal and then evaporated down and made up to a volume of 250 c.c. This was examined in a 200 mm. tube, and found to yield no appreciable rotation. About 200 c.c. of the liquid were, therefore, evaporated down to a syrup in a vacuum flask at a low temperature (in order to avoid the brown coloration of the liquid). This syrup, which, notwithstanding the above precaution, was of very deep colour, was examined in the 100 mm tube, when an indistinct rotation of +3° to +4° was observed.

4 c.c. of this syrup were then successively diluted with increasing proportions of water, and, on examination in the 100 mm. tube, the following rotations were obtained:—

Total volume of liquid.	Rotation.
6 c.c.	+2·5°
10 „	+1·0
18 „	+0·4
24 „	0·0
30 „	0·0
48 „	0·0

Thus, on the one hand, the right-handed rotation of this liquid was amply demonstrated, whilst, on the other hand, the inactivity of the 250 c.c. dilution examined above is duly accounted for.

We then proceeded to prepare the calcium salt of this right-handed acid by boiling with excess of calcium carbonate. After filtering, the liquid was concentrated to about one-third of its bulk, when, on cooling, an abundant crop of beautiful, colourless, transparent crystals was obtained. The mother liquor was poured off, and the crystals, after repeated washing with small quantities of iced water, were pressed between filter-paper.

A portion of this crystalline substance was then reduced to fine powder, and, after further carefully drying by pressure between filter-paper, was submitted to analysis, with the following result:—

I. 0·4585 gram yielded 0·2180 gram $CaSO_4$, corresponding to 13·98 per cent. calcium.

II. 0·2180 gram yielded, on combustion with CuO, 0·0975 gram OH_2 and 0·1695 gram CO_2 (the ash, on titration with N/10 HCl, was found to be pure $CaCO_3$), corresponding to H = 4·95 per cent., C = 21·19 per cent.

III. 0·2090 gram similarly yielded 0·0925 gram OH_2 and 0·1640 gram CO_2 (the ash on titration was found to contain a deficiency of CO_2 amounting to 0·0027 gram, which must thus be deducted from the CO_2 obtained), corresponding to H = 4·92 per cent., C = 21·05 per cent.

IV. 0·5835 gram lost 0·0725 gram on heating to 130° until constant = 12·43 per cent. H_2O.

	I.	II.	III.	Calculated for calcium glycerate, $(C_3H_5O_4)_2Ca,2OH_2$.
Ca.	13·98	—	—	13·98
C	—	25·38	25·26	25·17
H	—	4·95	4·92	4·89
O	—	—	—	55·96
				100·00
$2OH_2$	12·43	—	—	12·59 p. c.

There was thus no doubt that the crystalline substance obtained was a calcium glycerate. In order to ascertain its optical activity, 10 grams of the salt were dissolved in water and made up to 100 c.c.; this, on examination in the 1·984 decimetre tube, gave, at 14·4°, a rotation of $-2·4°$ (sp. gr. 1·048 at 14·4°, as against water = 1·000 at the same temperature), from which can be calculated by the formula

$$[\alpha]_D = \frac{100\alpha}{lc} \left(\begin{array}{l} l = \text{length of tube in decimetres,} \\ c = \text{concentration in grams per 100 c.c.} \end{array}\right)$$

the specific rotation. . . . $[\alpha]_D = -12·09$.

As it was thought possible that perhaps this active salt might be mixed with some of the inactive variety, we recrystallised a portion of the former and again determined the specific rotation by dissolving 1 gram of the salt in water and diluting to 10 c.c.; on examination in the 200 mm. tube, a rotation of $-2·4°$ was observed (temperature, 14·0°), a result which was thus identical with the former one.

It will be seen that this lævorotatory calcium salt was obtained from an acid liquid possessing a dextrorotatory activity, and it thus became of special interest to determine the rotation of the acid obtainable from the pure calcium salt. 2·724 grams of the salt (corresponding to 2·0 grams of free glyceric acid) were decomposed with the calculated quantity of oxalic acid, and, after filtering off the calcium oxalate, the filtrate was evaporated and made up to 10 c.c. On examination in the 1·984 decimetre tube at 12°, this gave a rotation of +0·85°, corresponding to a specific rotation of $[\alpha]_D = +2·14°$.

A second and equal quantity of calcium salt was similarly decomposed, and the resulting acid added to the first, the total volume being, as before, 10 c.c. On examination in the same tube at 12°, the rotation was found to be only +0·15°.

This result, that the double quantity of acid gave a much smaller rotation than the single, was extremely perplexing, but on again examining the tube containing the liquid six hours later, we found that the rotation had risen to +0 5° (temperature still 12°), and again, after 12 hours more, it was +0·5° to +0 6°.

It appeared, therefore, not improbable that this smaller rotation might be due to the formation of an anhydride during evaporation, which then gradually underwent hydration on standing in the presence of water. In order to test this point further, we took the above liquid, containing 4 grams of free acid, and diluted to 20 c.c.; this, on examination, was found to give no rotation. We now divided this liquid into two equal parts of 10 c c. each; one part was left at the ordinary temperature, and after six hours it was found to give a very slight rotation to the right, which had not materially changed after 12 hours more. It was then evaporated to a syrup and further heated for six hours on the water-bath; the residue was then extracted with water, but was found to be incompletely soluble, a considerable quantity of a white powder remaining; this was filtered off, and the filtrate, after dilution to 10 c.c., was examined in the 1 984 decimetre tube at 12°, and gave a rotation of −3·2°; after standing for 18 hours, the rotation was −3 0° (temperature, 11°).

The other half (measuring 10 c.c.) of the above inactive liquid was first digested for three and a-half hours on the water-bath, its volume being maintained throughout, and on then examining in the 1·984 decimetre tube at 13°, it gave a rotation of +0·5°; on examining again, after 18 hours, it had increased to +0·65° (temperature, 12°).

This portion was again digested for six additional hours on the water-bath, its bulk being maintained as before, and on then examining at 12·5°, it gave a rotation in the same tube of +0·8°, and this rotation still remained unchanged after the liquid had stood in the tube for 12 hours.

These remarkable phenomena admit of a ready and consistent explanation. In the first place, the new glyceric acid is itself indisputably dextrorotary, although we cannot yet assign an exact value for its optical activity, in consequence of the facility with which it passes, partially, at any rate, into an anhydride, which is strongly lævorotary. This relationship between the active glyceric acid and its anhydride is most conclusively demonstrated by the results of the two above experiments, in which, on the one hand, by digesting the acid with water, the dextrorotation was increased, whilst by prolonged heating of the acid to 100° a powerful lævorotation was obtained, and a considerable quantity of a white, insoluble body formed; the latter will, in all probability, prove to be the anhydride itself, whilst the lævorotation is doubtless produced by the portion of this anhydride remaining in solution, and far more than counteracting the feebler dextrorotation of any of the acid itself that may be present.

This explanation also easily accounts for the apparent discord between the activity of the free acid obtained in the preliminary experiments and that in the larger subsequent experiment, the former being lævo-, and the latter dextro-rotary, the salts in each case being, however, strongly lævorotary. In the preliminary experiments, the free acids, after being concentrated on the water-bath to the consistency of a syrup, were diluted to volume and immediately examined in the polarimeter; there would consequently be a considerable quantity of anhydride present, which, owing to its superior activity, would direct the rotation to the left. In the later and larger experiment, on the other hand, the solution of the free acid was carefully evaporated down at a low temperature in a vacuum flask (see p. 99), and the tendency to anhydride-formation must thus have been reduced to a minimum, with the result that the liquid exhibited a very considerable right-handed rotation.

The phenomena recorded above present the most perfect analogy to those observed by Wislicenus in his classical researches on paralactic acid (*Annalen*, 167, 302). Wislicenus found this acid to be dextrorotary,* whilst its salts (zinc and calcium) were lævorotary, the anhydrides again were most powerfully lævorotary, and their formation during the evaporation of the solutions of the acid prevented any accurate determinations of the specific rotation of the latter being made. Wislicenus further found that on diluting a solution of the acid, its dextrorotation is in the first instance diminished, and subsequently undergoes increase on standing, without, however, quite recovering its original value. This behaviour he explains by assuming that a hydrate, $C_3H_6O_3 + OH_2$, of inferior activity is formed. We have also found that the new glyceric acid also has its activity reduced by dilution (see p. 99).

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* Klimenko (*Journ. Russ. Chem. Soc.*, 12, 17; Beilstein, *Org. Chem.*, 1, 514), on the other hand, gives the specific rotation of paralactic acid as −2·4°.

We have more recently again fermented two large quantities, 60 grams respectively, of calcium glycerate, and have in both cases again recovered the crystalline lævorotary calcium salt from the fermented liquid.

We may point out, in conclusion, that the only attempt, as far as we are aware, hitherto made to break up ordinary glyceric acid into active varieties was that of Lewkowitsch, who, after his most successful decomposition of mandelic acid, endeavoured to apply the same methods to lactic and glyceric acids. By growing the mould *Penicillium glaucum* in a solution of ammonium glycerate, the liquid became lævorotary, but beyond this, the investigation was apparently not pursued (*Ber.*, 1883, 2720).

In conclusion we may summarise the more important results we have obtained as follows :—

(1.) In the fermentation of calcium glycerate by means of the *Bacillus ethaceticus* one half of the glyceric acid is destroyed, whilst the other half remains.

(2.) The glyceric acid so remaining after the completion of the fermentation is optically active, turning the plane of polarisation to the right.

(3.) The calcium and sodium salts of this active glyceric acid are, on the other hand, lævorotary.

(4.) The specific rotation of the calcium salt, $(C_3H_5O_4)_2Ca,2OH_2$, is $[\alpha]_D = -12{\cdot}09$.

(5.) Solutions of the acid, on prolonged heating on the water-bath, yield a considerable quantity of a white, insoluble, or sparingly soluble substance, whilst the solution from which this substance has separated is powerfully lævorotary.

(6.) There is every reason to believe that the sparingly soluble substance is an anhydride, and that it is powerfully lævorotary.

It is obvious that the acquisition of this new active acid opens out a wide field of interesting research in connection with the numerous derivatives that may be prepared from it, and to which we now propose to give our attention.

APPENDIX.

We have hitherto only very partially determined the specific properties of this active (lævorotary) calcium glycerate; it appears to be considerably more soluble in water than the inactive form, whilst, like the latter, it is insoluble in alcohol.

In investigating the fermentation products of calcium glycerate as described in the preceding communication, we found, however, the calcium salt of the residual acid to be soluble in alcohol, and this appeared to be out of harmony with the later observation of the insolubility of the pure salt. It appeared, however, that the presence of such a large quantity of calcium chloride amongst the fermentation products might very possibly affect the solubilities of the active and inactive calcium glycerates in alcohol. The following experiment was, therefore, made to ascertain this point:—

0·45 gram of active and inactive calcium glycerate respectively was dissolved in two separate quantities of water, and to each 0·385 gram of calcium chloride was added; each of these two solutions was evaporated to dryness on the water-bath, and then taken up with alcohol (90 per cent.); in both cases the entire residue at first dissolved, but on standing about 20 minutes, precipitation commenced, but rather more rapidly in the case of the inactive than in that of the active glycerate. The alcoholic liquids were allowed to stand for two days and then filtered, the precipitates were dissolved off the filters with water, and the calcium determined in each. The following quantities were obtained:—

Inactive Calcium Glycerate.	Active Calcium Glycerate.
0·0795 gram CaO, corresponding to 0·4042 gram calcium glycerate, or 90·24 per cent. of the quantity used.	0·0755 gram CaO, corresponding to 0·3856 gram calcium glycerate, or 83·81 per cent. of the quantity used.

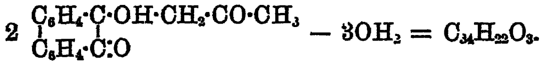
It thus appears that both the inactive and active calcium glycerates, and especially the latter, are appreciably soluble in alcohol in the presence of calcium chloride, and this partially accounts for the active calcium glycerate being found in the alcoholic solution of the fermentation products referred to, whilst the solubility would doubtless be considerably or even greatly increased through the other impurities which must have been present there also.

XIII.—*Condensation of Acetone-phenanthraquinone.*

By G. H. WADSWORTH, Associate of the Royal College of Science.

THE compound dehydracetone-phenanthraquinone (better *anhydracetone-phenanthraquinone*) was originally prepared by Japp and Miller (Trans., 1885, 17) by the action of an excess of strong aqueous potash on a mixture of phenanthraquinone and acetone. The yield of the compound was extremely small, and with the object of preparing it in quantity, I tried to obtain it from acetone-phenanthraquinone by the dehydrating action of sulphuric acid.

50 grams acetone-phenanthraquinone were very finely powdered and gradually added to a well cooled mixture of 500 grams of concentrated sulphuric acid and 500 grams of absolute alcohol, which was then gently heated to 45° on the water-bath. In a short time, the turbid liquid became clear, the acetone-phenanthraquinone having dissolved; but on cooling, a yellowish-brown substance separated in an amorphous condition. The separation was complete on allowing the mixture to stand over night. The amorphous substance was well washed with alcohol, afterwards with water, and finally dried at 100°. Most of the impurities were got rid of by a preliminary crystallisation from ether, the substance separating in hard, yellow cakes on the side of the beaker. The compound was then crystallised three times from benzene, after which it had a constant melting point of 238°. The substance is moderately soluble in benzene, from which it separates in hemispherical tufts of minute needles, but it is only sparingly soluble in glacial acetic acid, the compound having to be boiled for a considerable time before passing into solution. From the latter solvent, the compound separates in obliquely truncated prismatic needles. Various methods of applying the sulphuric acid have been tried, but the one described was found to give the best results. The result of the experiment was quite different from what was expected, for, on analysis of the compound, figures were obtained agreeing with the formula $C_{34}H_{22}O_3$, which can only be accounted for by supposing that 2 molecules of acetone-phenanthraquinone unite, with the elimination of 3 molecules of water, thus:—



$$2\begin{array}{l}C_6H_4\cdot C\cdot OH\cdot CH_2\cdot CO\cdot CH_3\\ C_6H_4\cdot C{:}O\end{array} - 3OH_2 = C_{34}H_{22}O_3.$$

	Substance.	CO_2.	OH_2.
I	0·2005	0·6276	0·0857
II	0·2024	0·6332	0·0866

	Calculated for $C_{34}H_{22}O_3$.		Found.	
			I.	II.
C_{34}	408	85·35	85·36	85·37
H_{22}	22	4·60	4·74	4·80
O_3	48	10·05	—	—
	478	100·00		

The yield of substance is very small, part of the original compound being decomposed into phenanthraquinone and acetone, a large quantity also being resinised during the reaction; on this account, no attempt has been made to determine the constitution of the body, which is probably very complex. Similar experiments were tried with acetone-benzil and diacetone-phenanthraquinone, but no definite compounds could be isolated.

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XIV.—*The Spectra of Blue and Yellow Chlorophyll, with some Observations on Leaf-green.*

By W. N. Hartley, F.R.S., Professor of Chemistry, Royal College of Science, Dublin.

It has long been known that leaf-green is composed of at least two colouring matters, called blue and yellow chlorophyll, the optical properties of which have been separately studied (G. G. Stokes, *Proc. Roy. Soc.*, **13**, 144; and H. C. Sorby, *ibid.*, **21**, 442). Chautard made an elaborate study of the spectra of mixed colouring matters of green vegetation (*Compt. rend.*, **75**, **76**, **77**); so also has Timiriazeff (*Ann. Chim. Phys.* [5], **12**, 355), and lately Reinke has studied very minutely the spectra of green living tissues (*Ber. deutsch bot. Ges.*, **1**, 395). The subject has further engaged the attention of Lommel (*Ann. Phys. Chem.*, **143**, 568), Schonn (*Ann. Phys. Chem.*, **144**, 166), Vogel (*Sitzungsberichte der K. Akademie, Munchen*, 1872, 133), Gerland, Wiessner, Filhol, Liebermann, Sachsse, and many others. A recent paper by Tschirch is published in the Trans., 1884, **45**, 57. The most recent researches are those of Schunck (*Proc. Roy. Soc.*, **39**, 348; **41**, 465; **42**, 184), which deal very largely with the decomposition product of chlorophyll called phyllocyanin, and its derivatives and combinations with basic substances and with acids. Also Wollheim (*Ann. Agronom.*, **14**, 141—143) has elaborately investigated such compounds (Abstr., 1888, 723). The colouring matters of green leaves are substances of a particularly interesting character, first, on account of the connection which seems now to have been established between the absorption spectrum of chlorophyll and its physiological functions, and, secondly, because of the intimate relation which must exist between its absorption spectrum and its chemical constitution.

While endeavouring to study the chemical constitution of chlorophyll, by means of its absorption spectrum, it has been found necessary to re-examine the substance, so as to establish the relationship between the visible and the ultra-violet spectra.* H. Becquerel has examined the action of an alcoholic solution of chlorophyll upon the infra-red rays, but he finds no strong band of absorption analogous to those in the luminous region (*Ann. Chim. Phys.* [5], **30**, 40). Abney, moreover, by his photographic process, has also failed to find any infra-red band.

The subject matter of this paper may be conveniently described under the following heads:—

a. Observations on the spectra of chlorophyll contained in living tissues.

b. The spectrum of the chlorophyll as seen in dried leaves.

c. Mode of extracting leaf-green unchanged, and separating the blue from the yellow chlorophyll.

d. Measurements of the spectra of the chlorophylls.

Observations on Living Tissues.

In order to ascertain how far the extracted colouring matters differed from, or were identical with those contained in living tissues, a series of observations were made upon green tissues, both by the visible and the ultra-violet spectra. In order to avoid the absorptive action for the ultra-violet rays which is known to be exerted by substances other than those which constitute the cellular tissue and the colouring matter of plants, it was considered desirable to make use of leaves not likely to contain any vegetable acids, aromatic substances, alkaloïds, or glucosides, and, accordingly, aquatic plants were chosen, *Anacharis* and a filmy green sea-weed being taken as examples. According to Sorby, yellow chlorophyll is absent from green sea-weeds. As the observations on living tissues did not give different results with different plants, whether ferns, of which some six species were examined, palms, three species, or ivy, two species, the character of the spectrum, as seen in the spring time, February, March, April, and May, may be briefly stated to be as follows :—The thickness of one leaf or frond showed the dark band overlying B, with an extension, consisting of a second weaker and closely-adjacent band, nearer the orange, and overlying C. There were no traces of a band in the yellow, close to D, and no indication of one in the green. The spectrum ended just beyond the magnesium green triplet *b*. Two thicknesses caused the bands to be much increased in density; there was no band, but only a dimness in the yellow at D; the green was practically unaltered, and the end of the spectrum was approached at *b* Three and four thicknesses transmitted no trace of red, but only the green and part of the yellow rays, no band was observed in the green at all. Care was taken that no alteration should be caused by exposing the colouring matter to a beam of light, concentrated by a lens, only the direct sun's rays or such as were reflected from a mirror, being employed. The leaves and fronds were pressed between plates of glass. No living green tissue of any kind was found to be capable of transmitting the ultra-violet rays. Ivy leaves, gathered in February, are so rich in green substances that even in strong sunlight one thickness transmitted nothing but the green rays, and showed no sign of any absorption band.

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* Since this paper was written, A. Hansen (*Die Farbstoffe des Chlorophylls*, 1889, p. 82) has examined the ultra-violet spectrum by Soret's method, but only incompletely.

The bands mentioned above are clearly shown in the diagrams representing the absorption curves of blue and yellow chlorophyll. The reason why the band I*b* in the red is not seen distinctly, but only as a çontinuation of I*a*, will be understood if a combination of the two curves is observed, as this shows the effect of the mixed chlorophylls. Overlying B and C there are actually three bands, two belonging to the blue, and one to the yellow chlorophyll.

A valuable abstract of a paper by Dr. Husemann appears in *Nature*. **30**, 224, for which we are indebted to Dr. C. A. MacMunn. It is there stated that yellow chlorophyll shows no fluorescence and no absorption band in the red, statements to the contrary being based on imperfect methods of separation. I think I shall be able to show that a yellow chlorophyll (that is to say, a yellow substance extracted from leaf-green), *containing no trace of the blue chlorophyll*, has a feeble but distinct and different band of absorption in the red, and a distinct fluorescence (see p. 118 and plate, p. 122). It is true that the band is very indistinct in an alcoholic solution, but this is by no means the case with the solution in benzene, if the solution be strong. When young leaves, gathered in the month of June from ivy, Virginia creeper, borage, rose trees, or blades of grass, are examined by sunlight, concentrated with a lens or concave mirror, the absorption band in the red is seen to occupy the space between B and C, and to overlie those lines, the termination of the spectrum being about wave-length 5000. Under the concentrated rays of the sun the tissues and the colouring matter are soon altered.

The Spectrum of Colouring Matters obtained from Dried Leaves.

To ascertain whether leaf-green is altered by drying, observations were made on *Anacharis* dried with blotting paper and subsequently heated in a water-bath to 100°; ivy leaves dried by exposure to dry air, and also over sulphuric acid in a vacuum; green sea-weed dried in a water-oven. Perfectly pure and dry ether, expressly prepared for the purpose, extracted in each case a green colouring matter, which showed two bands of absorption, one in the orange the other in the green, which I have not observed in living tissues. These are, however, figured in the beautiful drawings by Tchirsch, illustrating Reinke's paper (*Ber. deutsch. bot. Ges.*, 1, 14). These spectra were observed in leaves by means of a microspectroscope, and it is not unlikely that the bands were caused by an alteration in the colouring matter effected by exposure to intense light, but it is also possible that at the time of the year when the plants were examined a change had taken place in the colouring matter by a normal process. It appears that leaf-green also undergoes some chemical change when dried, even if the drying be effected in a vacuum at the ordinary temperature.

Mode of Extracting Leaf-green Unchanged, and of Separating the Blue from the Yellow Chlorophyll.

Solvents which are of service in separating blue and yellow chlorophyll are the following:—Light petroleum, benzene, chloroform, alcohol with not more than 2 per cent. of water, alcohol of 50 per cent., and dry ether. The hydrocarbons and chloroform dissolve the yellow chlorophyll in preference to the blue, when the colouring matter is dry. When chloroform has been used to make a solution, it should be distilled off as soon as possible, otherwise the colouring matter is apt to change in contact with air, and an absorption band appears in the green, the liquid becoming brownish. Turpentine is wholly unsuitable for the same reason, although at first the solution of blue and yellow chlorophylls is very brilliant. Hot turpentine yields a solution of an olive-green colour; on exposure to the air and diffused daylight, this is changed to a dull yellow, and finally becomes decolorised. A strong band of absorption in the green is seen in this solution. Other solvents of no particular interest are amyl alcohol, isopropyl alcohol, ethylene dibromide, and aldehyde.

To extract the colouring matter, ivy leaves were rolled into bundles and rasped on a bread-crumb grater, or minced finely with a knife on a chopping-board. Sometimes the shreds were steeped in cold water for 12 hours, whereby a good deal of a yellow or orange-yellow colouring matter was removed along with pectose, glucosides, and resin. As soon as no more of this colour was yielded to fresh water, the material was squeezed between linen cloths and folds of dry blotting paper. The colouring matter was then extracted by triturating with broken glass or fine quartz-sand in a porcelain mortar, together with the solvent to be used. When ivy leaves are boiled previous to extracting the colouring matter, and subsequent to washing with water, the shreds of leaf are of a dull olive-green in the centre and bluish at the edges. Extraction with cold alcohol then gives a solution showing the absorption band in the green strong, as in the turpentine solution; and no doubt the colouring matter has undergone a change.

When a solution of leaf-green is made with cold alcohol of 98 per cent., by extracting the colour from mixed ivy leaves, either with or without washing, its properties are seen to be those of the ivy leaf, in that it absorbs nearly all the red rays and the green rays near to the termination of the spectrum, the yellow and orange rays are dimmed, but the green is wholly transmitted. I prefer to extract the colour from the leaves immediately after mincing them, and as rapidly as possible, the whole of the green matter being immersed in spirit in a stoppered earthenware jar, and so protected from air and daylight.

To the alcoholic solution, a warm saturated solution of barium hydrate is then carefully added, until no further precipitation takes place, whereby a rich green precipitate is formed, leaving the solution yellow. After filtration and repeated washing on the filter with water and alcohol, which latter may be boiling, some of the yellow colouring matter still stains the filter. This is easily removable by washing with either cold or boiling chloroform. After a time, the washings begin to run with a greenish-yellow tinge. At this stage, the filter may be washed with boiled alcohol, and a repetition of the process causes the spirit to run through colourless. In order to separate the blue chlorophyll from the baryta compound, the precipitate is treated with a warm solution of boric acid in glycerin, to which alcohol is added, when a solution of blue chlorophyll is obtained. In this state it is very stable provided no acid be added to it; a few minutes boiling causes no alteration in its spectrum. It exhibits only two absorption bands in the red, very close to each other, the less refrangible being the sharpest in definition and the most intense; the spectrum ends in the blue.

A precisely similar substance is obtained by precipitating blue chlorophyll by the addition of water to an alcoholic solution of leaf-green, and shaking the liquid with benzene. In this case the benzene takes up the blue chlorophyll, while the yellow remains dissolved in the weak alcohol. This method of separation is similar to that first employed by Sorby. From the solution of yellow chlorophyll in weak alcohol, a portion of the spirit was distilled off, and the aqueous liquid was shaken with chloroform, which was separated and distilled; the substance was then redissolved by treating the residue with dry ether or with benzene.

A considerable quantity of a baryta compound of yellow chlorophyll was formed; this was of course separated by filtration, and the colouring matter was liberated by boric acid, as in the case of the bluish-green substance. It was proved that boric acid did not affect the spectrum of the yellow substance.

In filtering a large quantity of a strong alcoholic solution of leaf-green, it was noticed that there was a tendency in the yellow colouring matter to creep away from the blue chlorophyll. This separation of the two substances by the action of capillarity was promoted by using a filter 16 inches in diameter, and 2 inches too large for the funnel, and pouring the coloured solution at once on to the filter without previously moistening it. By this means a separation of the yellow substance was obtained, and its properties were studied. The portions of the filter stained yellow were removed, and treated with alcohol or ether, and the solution so obtained was submitted to the same reaction which the yellow chlorophyll had been subjected to on a larger scale; it was found that such treatment left it unchanged. Four preparations of blue chlorophyll and three of yellow chlorophyll were made from ivy leaves by the method described. Those specimens of the blue substance which I consider to be the purest were prepared from a well purified baryta precipitate, and gave a beautiful, red fluorescence. Two other specimens gave, one a brown, the other a chocolate-coloured fluorescence. The reason of this variation was ascertained, and it may be here stated that the true fluorescence is red.

The yellow chlorophyll in concentrated solutions in benzene or alcohol is brownish, its fluorescence is a magnificent red; a dilute ethereal solution of the yellow chlorophyll was seen to change from a yellow to a greenish-yellow in the bottle in which it was kept during the period it was under examination by the spectroscope; at last it became quite colourless. This specimen had been dissolved in ether which was not perfectly dry, and the trace of moisture may have promoted the change. The following reactions of blue and yellow chlorophyll are to be noted. *When the barium compound of blue chlorophyll is treated with an aqueous solution of boric acid, the substance instantly changes to a yellow colour upon boiling.*

Agitation with hydrochloric acid and ether yields with blue chlorophyll a brownish coloration in ether, and the blue characteristic colour in water. With a small quantity of the chlorophyll, there is no brownish coloration, and the ether remains colourless. When yellow chlorophyll is treated in a similar manner, the ethereal solution is yellow and the aqueous of a greyish tint. It appears, therefore, that the blue chlorophyll produces the blue colour in Frémy's reaction. When blue and yellow chlorophyll are separately treated with formic acid and ether, there are produced two new substances, showing absorption bands in the green.

M. Guignet has described a method of extracting the green colouring matter from leaves, and has recorded the existence of a definite crystalline compound of blue chlorophyll with sodium (*Compt. rend.*, **100**, 434). His preparations are made in the following manner:—Fresh leaves of spinach are treated repeatedly with boiling water containing ½ per cent. of soda crystals; in this way, tannin and pectose are removed. The residue is then strongly pressed and digested with alcohol of 95 per cent. If dried leaves are extracted with light petroleum, and subsequently with alcohol, the products are purer. He states that no blue chlorophyll is yielded to light petroleum, but only a mixture of the yellow and colourless matters. Finally, a small quantity of green colour is dissolved by the light petroleum.

My experience of the action of light petroleum upon air-dried, minced ivy leaves showed that at first there was extracted only a yellow chlorophyll; after a prolonged extraction a green substance became dissolved, and in forty-eight hours a deep-green solution was obtained, which showed two strong absorption bands in the green, and therefore did not consist of pure blue chlorophyll. The third extract was greenish-yellow; it showed only two contiguous absorption bands in the red, and a red fluorescence characteristic of yellow chlorophyll when mixed with a little blue. The fourth extract was at first, as nearly as possible, colourless, but in 12 hours it became yellow, with a very faint, greenish tinge; even the twelfth extract was yellow, and hitherto I have failed to get the solvent to remain colourless. The quantity of the solvent employed in this treatment amounted in all to at least 16 times that required to completely immerse the chopped dried leaves. On keeping the several extracts until a large accumulation should render it convenient to distil off the petroleum, the second solution of a greenish colour became bleached, probably by the action of light. Hence it appears that the action of light petroleum is not in all cases the same, and that this method is more conveniently applicable to the treatment of spinach than of ivy leaves, since the latter require to be cut up, if not minced finely. It was found that an alcoholic extract of fresh leaves became altered, notwithstanding that it was preserved in a bottle filled to the stopper, so as to leave not more than 1 or 2 c.c. of air-space in a litre of liquid, and in a fortnight, although the vessel was kept in a dark cupboard, the rich green tint had taken somewhat of an olive tinge, and the bands of absorption in the yellow and green were seen to be strongly developed (compare Russell and Lapraik, Trans., 1882, **41**, 334). Hence it is best first to extract freshly minced leaves without drying and with very strong alcohol, and then to precipitate the green colouring matter as rapidly as convenient. It might be advantageous to add a little ammonia to the alcohol, in order to neutralise any acid existing in the juices of the plant or likely to be formed by the oxidation of aldehydes. Russell and Lapraik have studied the changes in the chlorophyll spectrum caused by acids, &c. (*loc. cit.*).

The fresh extract of green leaves, and even that which has been kept for some little time, readily reduces nitrate of silver to a mirror when boiled in a flask, but as the quantity of reducing substances is very small, the mirror is thin. Hence, we may infer that the aldehyde is by keeping oxidised to formic acid, and that this alters the chlorophyll. Chlorophyll, altered by a trace of formic acid, is precisely like that altered by keeping.

The ivy leaves which had been treated 16 times with light petroleum were allowed to stand for some weeks with that solvent. The liquid acquired a deep olive-green colour. It was kept all the time in the dark, so that light could have had no effect upon it; air, too, was excluded.

Comparison of Various Chlorophyll Spectra.

Wave-length measurements of the bands visible in thick and thin layers of the solution are given on p. 114 (A). The bottles were then exposed to diffused daylight for a week; the contents of the small bottle lost much of the colour, and, indeed, the solution was only very faintly greenish in hue; its spectrum is shown (B).

Spectrum C is that of Tschirch's chlorophyll (Trans., 1884, **45**, 57). The process by which this, which was believed to be *pure chlorophyll*, was obtained, appears to have been previously described by Church and the substance itself is probably a zinc compound. Spectrum D is that of Russell and Lapraik's alcohol and ether-extract of various leaves. In spectrum A there were two bands' overlapping in the red, numbered I*a* and I*b*; of course, only the more refrangible edge of I*b* could be measured.

If a careful comparison be made of these measurements, it will be observed that in Tschirch's spectrum C, band I corresponds to bands I*a* and I*b*, and the same remark may be applied to Russell and Lapraik's

Comparison of Various Chlorophyll Spectra.

		Wave-length in millionths of a millimetre.						
		Red end of spectrum.	Red.		Orange.	Green.	Blue.	Blue.
			Overlapping bands.					
			Band I*a*.	Band I*b*.	Band II.	Band III.	Band IV.	Band V.
A. Colouring matter of ivy leaves, extracted with petroleum spirit. Air and light excluded.	-	739	695 - 656	—640	623—607	570—558	541—530	515 end
B. The same, a similar preparation	Thin layers	—	690—663	—	620—607	None	512—533	514—594
	Thick layers	—	685—658	—	620—606	570—557	540—533	511 end
C. Tschirch's preparation, probably a zinc compound.................. (Schunck, *Proc. Roy. Soc.*, 39, 360).	Thin layers	—	680—630	—	620—595	585—537	540—525	500 end
	Thick layers	—	685—	—	—	—555	535—520	510 end
D. Russell and Lapraik's alcohol and ether extract of green leaves.	—	—	678—610	—	628—600	580—573	545—532	510 end
Bands caused by the action of acids..	—	—	—	—	—	573—558	—	510 end
The same action, increased in intensity	—	—	—	—	—	—	544—532	

spectrum D, if allowance be made for the difference in strength of the solutions, and, above all, for the shifting of the bands, by reason of the solvents being different.

Band V, which has been observed by Krauss, does not seem to have been measurable in the preparations examined by Russell and Lapraik and by Tschirch. Band III in B seems to have been destroyed by exposure of the solution to the light. This band appears to have been present in Tschirch's substance, though the experiments of Russell and Lapraik show that it is caused by acids, which is entirely in accordance with my own observations, whether the acid be produced by oxidation of the aldehyde in the plant tissues, or in the chlorophyll extract, or whether the acid be added to the substance.

Both Tschirch and Russell and Lapraik seem to have regarded the overlapping bands I*a* and I*b* as only one band. Band I*b* appears to lie upon that due to yellow chlorophyll. Tschirch states that in his examination of living leaves he used sun-light concentrated by a lens, and passed the rays through two alum cells to intercept the infra-red spectrum, but he appears to have overlooked the fact that the violet and ultra-violet rays are capable of intense chemical action, and therefore it is rather doubtful whether the colouring matter did not undergo some change in the living tissue while under observation.

Measurements of the Spectra of the Chlorophylls.

The measurements which follow are those of the visible and of the ultra-violet region. The spectroscope used for the visible rays was furnished with a compound prism of Grubb's construction, capable of separating the two D lines; the telescope moved on a divided arc, and a pointer in the eye-piece, shaped like one of the nibs of a steel pen, that is, with one straight and one curved edge, served to fix the position of the bands. Readings were taken when the point and the straight vertical edge were no longer visible in an absorption band. The metallic lines in flame and spark spectra given in the British Association Report for 1878 were employed for converting arc measurements into wave-lengths and oscillation frequencies. The ultra-violet spectra were examined by a method already described (*Proc. Roy. Soc.*, **38**, 1). The absorption curve obtained from a solution in ether of colouring matter from dried *Anacharis* resembles that which may be drawn from Reinke's spectra (*loc. cit.*), with the addition of a feeble extension into the ultra-violet, which in very dilute solutions shows an absorption band. Specimens of blue and yellow chlorophyll were separately examined and absorption curves drawn from the measurements; the solutions of the three specimens of yellow chlorophyll were not of the same strength, and on this account. and from different solvents being used, the curves differ slightly.*

It is necessary to mention that it was proved by direct experiment that the solution of boric acid in glycerine, when mixed with an equal volume of alcohol, absorbed none of the ultra-violet rays less refrangible than wave-length 2200, so that solutions, which might contain these substances, could not be optically affected thereby.

Reinke (*Bied. Centr.*, 1884, 692—696; and Abstr., 1885, 48, 182) states that the spectra of living leaves and solutions of chlorophyll in alcohol were found to be somewhat different. Solutions of *fresh*

THE SPECTRUM OF BLUE CHLOROPHYLL.

Solution in Alcohol.

Thickness of layer of liquid.	Description of spectrum.	Oscillation-frequencies.	Wave-lengths.
5 mm.	Spectrum commences at	127	788
	Very strong absorption band	140—155	714—645
	Weak absorption band................	169—176	589—565
	Spectrum ends at	214	467
4 mm.	Spectrum commences at	130	764
	Very strong absorption band	139—147	719—678
	Weaker absorption band, almost continuous with the less refrangible band, but more diffuse......	149—157	669—637
	Very weak absorption band...........	169—175	589—570
	Spectrum ends at	214	465
3 mm.	Commencement in the red	132	755
	Strong absorption band	141—146	709—682
	Weaker absorption band, measurements rather doubtful	151—155	661—645
	Spectrum ends in the blue	215	463
2 mm.	Commencement in the red	133	749
	Absorption band	141—146	706—682
	Spectrum ends	218	
1 mm.	Commencement in the red	134	743
	Absorption band	142—145	701—686
	Termination in the blue about	222	450
	Rays feebly transmitted at..............	306	326
	and at	334	299

This solution was diluted five times; 2 c.c. were made up to 10 c.c.

* The curve of the alcoholic solution of yellow chlorophyll is represented in the plate, p. 122, by a dotted line.

leaves show no fluorescence; ordinary solutions, as is well known, do. Hence, he believes that the solutions change in properties by a disaggregation of the chlorophyll molecule. In the *Bot. Zeit.*, 1885, Nos. 5 and 9 (also Abstr., 48, 991), he shows that the maximum decolorising action of light on chlorophyll in alcohol and benzene lies between wave-lengths 650—610, between B and C, and the next between 450—410, which measurements agree with the relative intensities of the two most important and persistent bands, as shown by my curves, and which, therefore, correspond with vibrations of greatest amplitude at opposite ends of the spectrum.

Thickness of layer of liquid.	Description of spectrum.	Oscillation-frequencies.	Wave-lengths.
5 mm.	Commencement in the red	134	743
	Absorption band	141—144	706—692
	Visibility of rays terminates in the blue; rays photographed	208	480
	Very faint, not continuous	222	450
4 mm.	Commencement in the red	134	743
	Absorption band directly overlying C	145	689
	Rays transmitted to	208	480
	Faint and not continuous to	227	440
	Absorption band	227—277	440—361
	Rays transmitted, but not continuously, to	353	283
3 mm.	Commencement in the red	134	743
	Absorption band at C still visible	145	689
	Rays transmitted to	227	440
	Absorption band	227—251	440—398
	Rays transmitted, weak but not continuous, to	364	274
2 mm.	Commencement in the red	134	
	Rays fully transmitted to	208	480
	Rays continuous, but weak to	364	274
1 mm.	Commencement	134	
	Rays transmitted continuously to	364	274
	Rays not continuous at	370	270
	„ „ to	389	256
	Absorption band	389—433	256—231
	Spectrum ends at	433	231

The solution was again diluted five times; 2 c.c. were made up to 10 c.c.

Thickness of layer of liquid.	Description of spectrum.	Oscillation-frequencies	Wave-lengths.
5 mm.	Precisely the same as with 1 mm. of the previous solution.		
4 mm.	Commencement in the red	134	743
	Continuous spectrum, strong to	353	283
	„ „ weak to	364	274
	„ „ very weak to	389	256
	Absorption band	**389—413**	**256—242**
	Rays transmitted, but not continuous to end, at	442	226
3 mm.	The spectrum is continuous to	389	256
	Much weakened; it extends to	442	226
2 mm. 1 mm.	Spectrum becomes stronger, but is not of normal strength; it extends to	447	223

The solution was again diluted five times, and yet 1 mm. of the diluted solution only transmitted the ultra-violet rays feebly beyond 389 (256).

The absorption band seen in this solution between oscillation-frequencies 222 and 288, when 5 mm., 4 mm., and 3 mm. were examined, does not appear in the benzene solution of yellow chlorophyll, but a band appears between oscillation frequencies 226 and 246, but only at one thickness 2 mm. This might give rise to a suspicion that it is due to a slight admixture of blue chlorophyll with the yellow solution, but for the fact that, if it were, the absorption band in the red would be visible along with it.

The Spectrum of Yellow Chlorophyll.

Solution in Alcohol.

It must be noted that these spectra were measured in two halves, 1st, by the eye from A to beyond G, 2nd, by photography from F to beyond U. In such cases where the spectrum ends at about F, and the photographs show no rays between F or G and H, it is evident that an absorption band occurs, because the visible and the photographic spectra overlap to a considerable extent.

Thickness of layer of liquid.	Description of spectrum.	Oscillation-frequencies.	Wave-lengths.
15 mm.	Spectrum begins in the red between A and B	139	719
	Very weak absorption band, not easy to measure, the edges being too diffuse. Centre of band about C at	151	660
10 mm	Spectrum ends in the green at the B group, at	193	518
	Spectrum begins in the red	139	719
	Spectrum ends in the blue at	204	490
5 mm. 4 mm. 3 mm.	These are photographed spectra, and there is a very feeble transmission of some of the strong bright lines. Ill-defined absorption band, strong	193—213	518—467
2 mm.	Spectrum begins at (between F and G)	213	467
	Continued very feebly to	226	440
	Absorption band, strong	226—246	440—407
1 mm.	Continuous weak spectrum from near F	208	480
	to	389	256
	This solution was diluted five times; 2 c.c. was made up to 10 c.c.		
5 mm. 4 mm. 3 mm.	A continuous weak spectrum to	389	256
2 mm.	Continuous spectrum weak to	433	231
1 mm.	„ „ strong to	353	283
	„ „ weak to	442	226

Solution in Alcohol. Another Preparation.

20 mm.	Spectrum begins in the red at	139	719
	Weak absorption band	149—152	670—658
	Spectrum ends in the green	199	502

THE SPECTRUM OF YELLOW CHLOROPHYLL.

Solution in Benzene.

Thickness of layer of liquid.	Description of spectrum.	Oscillation-frequencies.	Wave-lengths.
15 mm.	Red rays commence between A and B	139	719
	Weak absorption band from near B to C	144—151	694—660
	Visible spectrum ends near E in the green	188	530
5 mm. 4 mm. 3 mm.	No absorption from near B to C visible. Rays transmitted as far as the green, but all beyond absorbed.		
2 mm.	All rays beyond the green absorbed with the exception of certain strong lines in the ultra-violet.		
	Absorption band from near E to near M	188—264	530—378
	Spectrum weakly transmitted from between K and M	264	378
	to beyond U	353	274
1 mm.	Feebly continuous spectrum from	264	378
	to	364	274
	This solution was diluted five times; 2 c.c. was made up to 10 c.c.		
5 mm. 4 mm. 3 mm.	The same effect as with 1 mm. above, the spectrum increasing in strength progressively.		
2 mm.	Spectrum begins feebly at	213	467
	and extends to	370	270
1 mm.	Spectrum begins a little beyond F at......	208	480
	and extends to......	370	270
	This solution was diluted five times; 2 c.c. was made up to 10 c.c.		
5 mm. 4 mm. 3 mm.	The same effect as with 1 mm. above.		
2 mm. 1 mm.	Spectrum feebly visible at	208	480
	Continuous, fairly strong, from	277	361
	,, ,, ,, to	308	324

THE SPECTRUM OF YELLOW CHLOROPHYLL.

Solution in Ether.

Thickness of layer of liquid.	Description of spectrum.	Oscillation-frequencies.	Wave-lengths.
20 mm.	The spectrum was the same as that measured from the solution in benzene.		
	Red rays begin between A and B	139	719
	Weak absorption band from near B to C	144 - 148	694—670
	Spectrum ends in the green near E at	188	530
5 mm.	No spectrum transmitted in the blue, violet, or ultra-violet ends at	206	
4 mm.	ends at	214	
3 mm.	A faint, discontinuous spectrum, ends at ..	221	
2 mm.	Spectrum commences on the photographs at	213	467
	Continuation *very feeble* to..............	226	440
	Absorption band from between F and G to H..............................	226—251	440—398
	Rays transmitted, but not continuously, to	307	325
1 mm.	Weak continuous spectrum to	288	346
	The original solution was diluted five times; 2 c.c. made up to 10 c.c.		
5 mm.	The same effect as with 1 mm. above.		
4 mm.	Continuous spectrum, weak to	288	325
3 mm.	The same.		
2 mm.	Continuous spectrum, weak to	308	324
1 mm.	Continuous spectrum, weak to	353	283
	This solution was diluted five times; 2 c.c. made up to 10 c.c.		
5 mm.	The same as with 1 mm. above.		
4 mm.	" " "		
3 mm.	Continuous spectrum, weak to	370	270
2 mm.	The same.		
1 mm.	Continuous spectrum, weak to	433	231

This solution, which originally was prepared with absolute alcohol, was of a deep yellowish-brown colour; it was evaporated to dryness in a vacuum and taken up with ether. Its brownish colour remained for a few days, but during examination by sunlight, it became a greenish-brown, later of a pale-green, and finally it became decolorised.

The yellow chlorophyll has an absorption band in the orange-red, and a very powerful absorption of all rays beyond the *b* group. When very thin layers of a dilute solution are examined, there is a powerful absorption band extending from *b* to K. The absorption band in the orange-red is different from either of those belonging to blue chlorophyll, and the curves offer further evidence that the specimens of yellow chlorophyll were quite free from any admixture of the blue, because, if they had not been so, the least refrangible and most persistent absorption band of the latter would have been visible. It is only the *alcoholic* solutions of blue and yellow chlorophyll which are strictly comparable, because the displacement of the bands by the difference in the refraction index of the solvents interferes with the comparison of a solution in alcohol with one in benzene or ether even of the same substance. But in all three spectra there is a powerful band of absorption extending from the *b* group to K, even in thin layers of a weak solution. In thick layers, no rays beyond *b* are transmitted.

It will be seen that the leading characteristics of unaltered leaf-green are those of blue chlorophyll, namely, an intense absorption in the red, somewhat stronger even than in the violet and ultra-violet.

We learn from the absorption bands that the vibrations within the molecule of the blue chlorophyll are both of the slowest and the most rapid, and that they are also of very great amplitude.

The rays transmitted by leaf-green, namely, the yellow and green, are barely capable of any photochemical action either on silver salts or organic substances. Such rays, therefore, are not likely to be effective in decomposing carbonic acid.

Blue chlorophyll, judging from its chemical composition and its spectrum, is very probably a derivative of a benzenoïd hydrocarbon. It is certainly neither a wax, a fatty acid, a carbohydrate, nor an albuminoid from grain, nor, in fact, any other substance derived from an open chain of carbon atoms.

It has been clearly established by the experiments of Lommel, Timiriazeff (*Compt. rend.*, **100**, 851), Reinke (*Bot. Zeit.*, 1885, Nos. 5 and 9), Bonnier and Mangin (*Compt. rend.*, **102**, 123), and Paul Bert (*Compt. rend.*, **87**, 695), that the rays absorbed by blue chlorophyll are those which are necessary to plant life, and which cause plants to grow; and that plants die when they can get no other daylight than such as has passed through a weak solution of chlorophyll.

By Regnard (*Compt. rend.*, **101**, 1293), and also Timiriazeff (*Compt. rend.*, **102**, 686), it has been shown that outside the cell walls, a colourless substance derived from chlorophyll by the action of nascent hydrogen, chlorophyll is capable of decomposing carbonic acid when exposed to light. Regnard showed that even wool dyed with chlorophyll is capable of liberating oxygen from carbonic acid.

It seems, therefore, that the molecule of chlorophyll, or one of its

RTLEY

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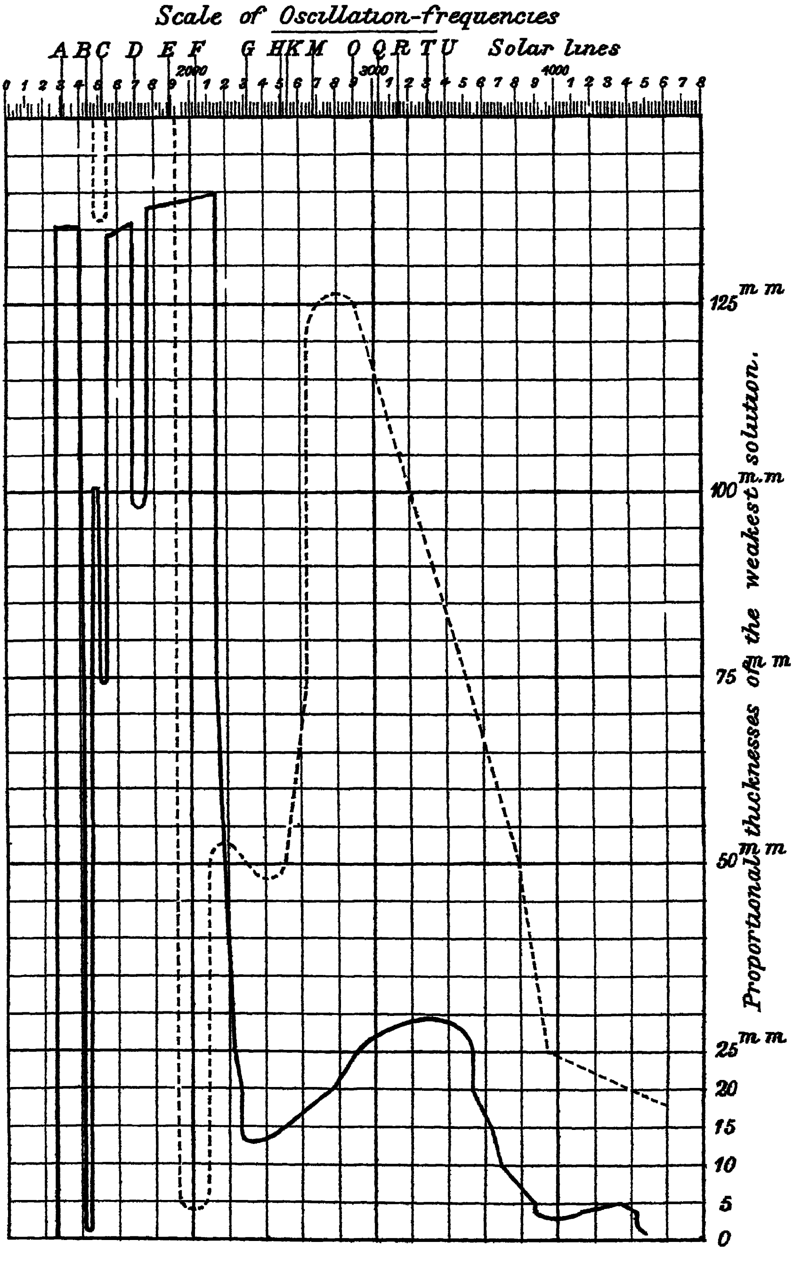
ABSORPTION CURVE OF BLUE CHLOROPHYLL ALCOHOLIC SOLUTION

The dotted line indicates the curve of yellow chlorophyll.



transformation products, is actually capable of reducing carbonic acid.

From the researches of Gerland and Rauwenhoff, and especially Reinke, it is known that leaf-green contains some aldehydic substance, and that formic aldehyde is constantly present in living green tissues. As formic aldehyde is the first product when a molecule of oxygen is removed from carbonic acid,

$$H_2CO_3 - O_2 = H_2CO,$$

and as it is very easily polymerised and converted into a sugar, its further conversion into starch $10(H_{20}C_{12}O_{10})$ by the removal of 20 mols. of water is easily understood by all who are familiar with the chemistry of the carbohydrates. Such a course of chemical change is not a purely speculative one, for E. Laurent has shown that the etiolated shoots of potatoes, when kept in the dark, can form starch from glycerol, and carbohydrates of the glucose and saccharose groups. Moreover, a glucoside has actually been separated from chlorophyll. Baeyer discovered a series of substances formed by the union of aldehydic compounds, and particularly formic aldehyde with aromatic derivatives of the most diverse nature (*Ber.*, **5**, 1094; and **6**, 220). I have shown the probability of the chlorophylls being aromatic substances, and we can thus understand how they could combine with formic aldehyde; therefore it is quite intelligible how such a combination could be split up into a sugar or starch, and chlorophyll.

R. Sachsse supposes that chlorophyll is the first product of the reduction of carbonic acid, and this is itself converted by further change into starch and other carbohydrates. It is difficult to conceive of even the bare possibility of this, but there is no difficulty in reconciling the evidence which has led to this conclusion with facts consistent with a process which I have here sketched in outline.

The first step in the reduction of carbon dioxide or of carbonic acid, H_2CO_3, is a process of dissociation, for it has been observed by Godlewski that in a bright light an increase of carbon dioxide in the air, up to 8 per cent., causes a rapidity in the formation of starch which is fourfold the ordinary amount. In other words, the rate of chemical change (starch formation) appears to be a function of the intensity of the light and the pressure of the carbon dioxide, and inversely as the pressure of the oxygen The formation of starch under these conditions is a photographic process, that is to say, one dependent on radiant energy, acting upon carbonic acid.

Latterly, Hansen (Abstr., 1888, 867) states that the colouring matter of leaves absorbs carbon dioxide, and forms an unstable compound therewith; the absorption increases with the rise of temperature and the pressure of the gas. He believes that the chlorophyll, after it has combined with the CO_2, hands it over to the plasma of the chlorophyll grains. It is, however, much more probable, on chemical grounds, that the compound of chlorophyll with carbon dioxide is entirely decomposed, first, by the elimination of oxygen, and secondly, by the elimination of water, so that there are successively formed compounds of chlorophyll (1) with carbon dioxide; (2) with formic aldehyde; (3) with glucose; and finally, starch, completely formed, is split off the molecule.

NOTES.

(1.) According to Draper, Sachs, Pfeffer, and Gerland, the curve of assimilation is in the green and yellow. Later experiments, as, for instance, those of Timiriazeff, show that it is in the red overlying B. Paul Bert's experiments conclusively prove that it is not in the green and yellow.

(2.) When one compound enters into combination with another, the resulting molecule may be altogether different in its mode of vibration, and become susceptible of decomposition by vibrations to which it was previously insensible; the evidence of this is afforded by organic bases and their salts; thus, molecular weights of para-toluidine and hydrochloric acid when submitted to the action of rays lying between the red and extreme ultra-violet yield a spectrum which is that of the base alone, for the hydrochloric acid has no action on these rays; but when the molecules are combined, the spectrum is greatly modified.

(3.) Some writers have apparently considered vibrations of great wave-length as vibrations of great amplitude. They are not necessarily so. Vibrations of great wave-length are slow vibrations, but they may be either of large or small amplitude. Amplitude is measured by the *intensity* of *the rays*. Amplitude in the vibrations of a molecule is measured by the *intensity* of *the absorption* of the rays.

(4.) Reinke has calculated the rate of vibration of the molecule or of the atomic group within the molecule which causes the reduction of carbonic acid. This is an application of the method by which I calculated the rates of vibration of the molecules of ozone, benzene, naphthalene, and anthracene. Reinke's calculations are to some extent inaccurate, inasmuch as the absorption of the ultra-violet rays has not been taken into account.

(5.) It will be recollected that according to Pringsheim the function of chlorophyll is merely a physical one, due to its colour. It acts as a screen, diminishing the intensity of the light, and thereby the amount of oxidation in the cell ("Researches on Chlorophyll," *Quarterly J. Micr. Sci.*, 1882, 110). If this were correct, any other green screen would answer the purpose, and best of all would be a solution of chlorophyll; but it has been shown that under such protection plants die.

(6.) To be strictly accurate 0 should be added to the number in the columns headed "oscillation-frequencies." W. N. H.

XV.—*The Molecular Volumes of the Saturated Vapours of Benzene and of its Halogen Derivatives.*

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IN a previous paper (Trans., 55, 1889, 486), an account was given of determinations of the molecular volumes of benzene and of its monohalogen derivatives in the liquid state, and it was pointed out that certain simple relations are to be observed between the boiling points, vapour pressures, and molecular volumes of the four substances fluorbenzene, chlorobenzene, bromobenzene, and iodobenzene; when any one of these substances, however, is compared with benzene, the corresponding relations are not so simple.

Briefly recapitulated, the relations between the halogen derivatives of benzene are as follows:—

1. When the four substances are compared at their boiling points under equal pressures, these temperatures—on the absolute scale—and also the corresponding molecular volumes, bear a constant ratio to each other, whatever the pressure.

2. The critical pressures of fluorbenzene and chlorobenzene, and in all probability those also of bromobenzene and iodobenzene, are equal.

3. The relations of Van der Waals, as regards "corresponding" temperatures, pressures, and volumes of liquid hold good accurately in the case of the halogen derivatives of benzene, but since the critical pressures are equal, *corresponding* pressures are in this case *equal* pressures.

4. A comparison of benzene and fluorbenzene showed that whereas at corresponding pressures the boiling points, measured on the absolute scale, are far from showing a constant ratio to each other, yet when the molecular volumes of these substances are compared either at corresponding temperatures or at corresponding pressures, the ratios of the volumes are nearly constant, though the two methods of comparison are not equivalent and necessarily give somewhat different results.

It has been pointed out by Professor Orme Masson (*Phil. Mag.*, November, 1890) that when the halogen derivatives of similar hydrocarbons are compared together at their boiling points under normal pressure, their molecular volumes bear the same ratio to each other as the boiling points (expressed on the absolute scale), but that inorganic compounds, even when closely related, do not, as a rule, exhibit such simple relations.

In a short paper published in the same number of the *Phil. Mag.* (p. 423), I showed that Orme Masson's relation is really a special case of a more general one which should be applicable to all substances if the generalisations of Van der Waals were strictly true. This relation may be expressed as follows:—The molecular volumes of any two substances, both in the liquid state and as saturated vapour, at their boiling points under "corresponding" pressures *should be* directly proportional to their absolute critical temperatures and inversely proportional to their critical pressures; or

$$\frac{V}{V'} = \frac{v}{v'} = \frac{T}{T'} \times \frac{p'}{p}.$$

where V and V′ are the molecular volumes of the liquids, v and v' the molecular volumes of their saturated vapours, T and T′ the absolute critical temperatures, and p and p' the critical pressures.

When the critical pressures are equal (as in the case of the halogen derivatives of benzene, and possibly also of some of the groups of halogen compounds cited by Orme Masson), corresponding pressures become equal pressures, and we then have the simple law:—The molecular volumes of the members of any group of chemically related compounds whose critical pressures are equal, measured at their boiling points under any equal pressure, are directly proportional to their absolute critical temperatures, and therefore to their absolute boiling points under any equal pressures; or

$$\frac{V}{V'} = \frac{v}{v'} = \frac{T}{T'}.$$

The wider generalisation appears to be approximately true for the liquid state for nearly related substances whose critical pressures are different; in the case of benzene and fluorbenzene, for instance, the difference between the observed and calculated molecular volumes is very little over 1 per cent., but considerable differences are in some cases to be observed when the substances are not closely related, and even when the higher alcohols are compared with methyl alcohol.

The experimental work described in the present paper was undertaken in order to find whether the relations which have been shown to hold good for the molecular volumes of the liquids are also applicable to those of the saturated vapours.

The method employed was that recently described to the Society (this vol., p. 37), but, as the molecular volumes of the liquids had already been carefully determined, it was only necessary to measure the volume of liquid and of saturated vapour at each temperature when the whole tube was heated.

The ratio of the specific volume of the saturated vapour to that of the liquid at any temperature is given by the equation

$$r_T = \frac{V_c}{V_T - V'_T},$$

where V_T is the true volume of liquid, supposing all vapour to be condensed, and V_c and V'_T are the observed volumes of saturated vapour and of liquid. The values of V_T were calculated from the molecular volumes previously determined.

The observed values of V'_T were mapped and curves drawn through the points; the values read from these curves, which differed, however, very slightly from the observed values, were employed in the calculations.

The specific volumes of the saturated vapour are given by the equation $s_T = r_T \times S_L$, where S_L is the specific volume of the liquid at T°. The molecular volumes of the saturated vapours $= v_T = Ms_T$, where M is the molecular weight of the substance.

Before describing the results obtained, it may be well to point out the chief sources of error which are likely to occur.

1. *Errors of Reading.*—Since in the formula $r_T = \frac{V_c}{V_T - V'_T}$ the volume ratio r_T, and therefore the molecular volume depends on the difference between two volumes of liquid V_T and V'_T, any small error in the determination of either of these values will introduce a relatively large error in the calculated value of the molecular volume. It is important, therefore, to find what accuracy in reading has usually been attained, and to get some idea of the influence of the errors of reading on the molecular volumes.

A fair test of the accuracy attained is afforded by the determinations of the weights of the various quantities of liquid employed, for the weights were calculated in each case from the results of volume readings at several different temperatures, and therefore the differences of the individual values from the means afford the required data. There are in all 47 readings, giving nine weight determinations. The differences of the individual weight determinations from the mean values correspond to errors in reading of volume, and these errors are tabulated below.

TABLE I.

Number of readings.	Errors in reading.
1	between 0·15 and 0·2 mm.
1	„ 0·1 „ 0·15 „
5	„ 0·05 „ 0·1 „
40	less than 0·5 mm.

It will be seen, therefore, that the error of an individual reading is rarely so great as 0·1 mm.

In the tables of results, I have given in each case the percentage error in the molecular volume corresponding to an error of 0·1 mm. in the reading of the volume of liquid. These columns are headed E in the tables. Errors in the calibration of the tubes and in the previous determinations of the molecular volumes of the liquids would similarly affect the values of the molecular volumes of the saturated vapours.

Effect of Air or permanent Gas in Tube.—Although the amount of saturated vapour in a given space is theoretically independent of the presence or absence of a permanent, indifferent gas, yet, in practice, there can be no doubt that the presence of such a gas does influence the results, inasmuch as it increases the time that elapses before the space above the liquid becomes completely saturated with vapour. To take an extreme case, suppose that the whole tube is at first at a constant temperature, t°, at which the vapour pressure of the liquid is extremely small and practically negligible; and that the tube is then raised to a much higher temperature, T°. Vapour will be evolved from the surface of the liquid, and, the tube being very narrow, the air will be driven forward and will occupy the upper part of the tube, the effect being at first the same as if the tube were shortened. The amount of vapour evolved will therefore be too small, and if readings are taken too quickly, the observed volume of liquid, V'_T, will be too great. In course of time, the air will diffuse through the vapour, and if there were no other disturbing factor a correct result would finally be obtained; but if saturated, or nearly saturated, vapour be allowed to remain for a considerable time at a constant temperature, there is danger of condensation taking place to a slight extent on the walls of the tube, and I have observed that the presence of a permanent gas tends to cause such condensation. Any variations of temperature, even if very minute, would increase this danger.

It is, therefore, of great importance that air should be expelled from the tube as completely as possible; and, in fact, one set of observations was rendered inaccurate owing to the incomplete expulsion of air. Moreover, bromobenzene appears to undergo slight decomposition at temperatures above 240° or 250°, a small amount of permanent gas being formed; and it was found that whereas up to 240° the readings of volume became constant almost immediately, at higher temperatures the alteration of volume did not cease until the tube had been kept at a constant temperature for from 10 to 20 minutes. The determinations of the molecular volumes of the saturated vapour of bromobenzene above 250° are also irregular and obviously inaccurate, a slight deviation from the curve being noticeable even at 250°.

Effect of Impurity of Jacketing Vapour.—If the substance employed to heat the tube were impure, the temperature of its vapour would be higher at the bottom than at the top of the tube. Such a difference of temperature, even if very slight, would cause evaporation of liquid in the volume tube and condensation in the upper part of the tube. This would make it quite impossible to obtain accurate results, but errors due to this cause could hardly fail to be detected, and they were certainly absent from my results.

Two tubes were employed in these experiments: in the first, A, the volume of saturated vapour was from 8 to 12 times as great as that of the liquid; in the second, B, the volume of saturated vapour was about twice as great as that of the liquid. The volumes of liquid were read at 0° and at two or three temperatures between 8° and 15°, and, after correction, when necessary, for the small amount of substance present as saturated vapour, the weights were calculated from the known molecular volumes of the liquid at the observed temperatures. The weight determinations are given in the table below.

Substance.	Tube.	Temp.	Volume of liquid.	Molecular volume.	Weight.	
Fluorbenzene....	A	0·0°	·2000	91·54		·2093
,, ...		8·5	·2020	92·45		·2093
,, ...		11·1	·2025	92·73		·2092
,, ...		12·3	·2028	92·85		·2093
,, ...		14·5	·2032	93·08		·2091
					Mean..	·20924
Fluorbenzene....	B	0·0°	·3869	91·54		·4050
,, ...		10·45	·3915	92·65		·4048
,, ...		11·9	·3924	92·82		·4050
					Mean..	·40493
Chlorobenzene...	A	7·3°	·1845	100·18		·2067
,, ...		8·25	·1846	100·27		·2066
,, ...		10·7	·1850	100·51		·2065
,, ...		11·2	·1851	100·56		·2065
,, ...		13·4	·1855	100·77		·2066
					Mean..	·20660
Chlorobenzene...	B	0·0°	·3681	99·48		·4152
,, ...		10·8	·3720	100·50		·4153
,, ...		11·7	·3722	100·58		·4152
,, ...		12·8	·3734	100·70		·4160
,, ...		14·0	·3734	100·81		·4156
					Mean..	·41530*

* The observation at 12·8° was omitted in calculating the mean weight.

Substance.	Tube.	Temp.	Volume of liquid.	Molecular volume.	Weight.
Bromobenzene ...	A	0·0°	·2408	102·90	·3665
„		9·55	·2430	103·76	·3667
„		11·7	·2432	103·96	·3663
„		12·2	·2433	104·00	·3663
„ ..		13·7	·2435	104·13	·3662
„		14·75	·2437	104·23	·3662
„		15·35	·2439	104·30	·3662
					Mean.. ·36635
Bromobenzene ...	B	0·0°	·3395	102·90	·5167
„		8·8	·3422	103·69	·5168
„ ...		12·5	·3434	104·04	·5169
„		14·5	·3440	104·21	·5169
					Mean.. ·51682
Iodobenzene	A	5·0°	·1870	109·75	·3466
„		6·7	·1870	109·90	·3461
„		7·6	·1872	109·98	·3463
„		8·2	·1872	110·03	·3461
„		9·3	·1874	110·13	·3462
„		9·8	·1875	110·17	·3463
„		9·8	·1876	110·17	·3464
„		10·6	·1878	110·25	·3464
					Mean.. ·34630
Benzene	A	0·0°	·1892	86·48	·1703
„		7·3	·1907	87·23	·1702
„		11·3	·1918	87·67	·1703
„		13·4	·1921	87·88	·1702
„		14·6	·1923	87·99	·1701
					Mean.. ·17022
Benzene	B	0·0°	·3363	86·48	·3027
„		6·9	·3394	87·19	·3030
„		9·5	·3403	87·46	·3029
„		10·6	·3407	87·57	·3028
„		12·0	·3413	87·73	·3028
					Mean.. ·30284

The actual determinations of the molecular volumes of the saturated vapours are given in the following tables. The data given are—

T. The temperature of the tube.

V_c. The observed volume of vapour.

V_T. The true volume of liquid, supposing all vapour to be condensed. These values were calculated from the known specific volumes of the liquids.

V'_T. The observed volume of liquid.

r_T. The ratio of the specific volume of saturated vapour to that of liquid at T°.

v_T. The molecular volume of the saturated vapour at T°.

E. The percentage error corresponding to a hypothetical error of 0·1 mm. in the reading of volume.

T° C.	V_c. c.c.	V_T. c.c.	V'_T. c.c.	r_T.	v_T. c.c.	E. p.c.
Fluorbenzene. Tube A.						
80	2·3374	·2204	·2133	329·0	33200	3·1
90	2·3377	·2234	·2138	244·0	21900	2·3
100	2·3383	·2266	·2139	184·0	19100	1·8
110	2·3396	·2299	·2132	140·0	14750	1·3
120	2·3418	·2355	·2117	107·5	11500	1·0
130	2·3418	·2374	·2093	83·5	9070	0·8
140	2·3490	·2114	·2058	66·0	7290	0·6
150	2·3544	·2456	·2010	52·8	5940	0·5
Fluorbenzene. Tube B.						
130	·8883	·4594	·4486	82·30	8940	3·5
140	·8839	·4672	·4534	64·10	7080	2·7
150	·8794	·4753	·4582	51·40	5780	2·2
160	·8740	·4841	·4631	41·70	4770	1·8
170	·8704	·4936	·4680	34·00	3970	1·5
180	·8659	·5038	·4 28	27·95	3330	1 2
190	·8621	·5153	·4770	22·50	2745	1·0
200	·8583	·5277	·4811	18·42	2300	0·8
210	·8548	·5415	·4849	15·10	1935	0·7
220	·8519	·5573	·4882	12·33	1626	0·6
230	·8501	·5755	·4903	9·98	1359	0·5
210	·8192	·5966	·4916	8·09	1141	0·4
250	·8503	·6228	·4908	6·44	949	0·3
260	·8548	·6566	·4866	5·03	781	0·2
270	·8681	·7057	·4731	3·74	624	0 2
275	·8838	·7414	·4582	3·12	517·5	0·1
280	·9172	·7891	·4249	2·52	470·2	0·1
Chlorobenzene. Tube A.						
130	2·4297	·2099	·2015	289·0	33000	2·6
140	2·4303	·2125	·2017	225·0	26000	2·0
150	2·4312	·2152	·2015	177·0	20700	1·6
160	2·4328	·2179	·2006	141·0	16600	1·3
170	2·4351	·2208	·1990	112·0	13400	1·0
180	2·4380	·2239	·1968	90·0	10900	0·8
190	2·4417	·2272	·1938	73·1	9020	0·6
200	2·4464	·2307	·1897	59·7	7480	0·5
210	2·4529	·2344	·1839	48·6	6180	0·4

T° C.	V_c c.c.	V_T c.c.	V'_T c.c.	p_T	v_T c.c.	E. p.c.
			Chlorobenzene. Tube B.			
160	·9050	·4381	·4317	141·00	16700	5·9
170	·9010	·4439	·4360	114·00	13700	4·9
180	·8971	·4501	·4403	91·00	11100	3·9
190	·8931	·4567	·4446	74·00	9100	3·2
200	·8892	·4637	·4489	60·00	7500	2·6
210	·8853	·4712	·4531	49·00	6200	2·1
220	·8816	·4790	·4572	40 50	5250	1·7
230	·8777	·4875	·4614	33·60	4430	1·5
240	·8740	·4968	·4654	27·80	3740	1·2
250	·8705	·5068	·4693	23·20	3180	1·0
260	·8674	·5179	·4727	19·20	2680	0·8
270	·8645	·5301	·4759	15·95	2280	0·7
275	·8634	·5359	·4772	14·45	2100	0·7
280	·8622	·5410	·4786	13·18	1938	0·6
			Bromobenzene. Tube A.			
160	2·2980	·2819	·2726	247·0	29800	2·4
170	2·2978	·2852	·2735	196·0	23900	1·9
180	2·2980	·2886	·2740	157·0	19400	1·5
190	2·2987	·2922	·2740	126·0	15800	1 2
200	2·3000	·2960	·2734	102 0	12900	1·0
210	2·3015	·3000	·2725	83·7	10700	0·8
220	2·3039	·3042	·2708	69·0	8970	0·7
230	2·3071	·3087	·2683	57·1	7540	0·5
240	2·3115	·3134	·2645	47·3	6330	0·4
			Bromobenzene. Tube B.			
190	·9511	·4123	·4049	129·0	16100	5·1
200	·9479	·4176	·4085	104·0	13200	4·2
210	·9447	·4232	·4120	84·0	10800	3·4
220	·9414	·4292	·4157	70·0	9070	2·8
230	·9383	·4354	·4191	57·5	7600	2·3
240	·9355	·4421	·4223	47·2	6330	1·9
250	·9330	·4491	·4251	38·9	5290	1·6
260	·9308	·4569	·4276	31·8	4400	1·3
270	·9290	·4653	·4298	26·2	3700	1·1
280	·9272	·4746	·4319	21·7	3120	0·9
			Iodobenzene. Tube A.			
190	2·3756	·2214	·2124	264·0	34300	2·5
200	2·3759	·2239	·2127	212 0	27900	1·9
210	2·3766	·2264	·2126	172·0	22900	1·6
220	2·3779	·2290	·2121	141·0	18900	1·3
230	2·3796	·2317	·2111	115·5	15700	1·1
240	2·3816	·2345	·2097	96·0	13200	0·9
250	2·3845	·2375	·2074	79·2	11050	0·7
260	2·3885	·2407	·2041	65·3	9230	0·6
270	2·3932	·2441	·2000	54·3	7780	0·5
280	2·3987	·2478	·1952	45·6	6640	0·4

T° C.	V_c. c.c.	V_T. c.c.	V'_T. c.c.	r_T.	v_T. c.c.	E. p.c.
			Benzene. Tube A.			
80	2·3875	·2090	·2010	298·0	28500	2·8
90	2·3881	·2118	·2012	225·0	21800	2 0
100	2·3894	·2148	·2007	169·0	16600	1·6
110	2·3910	·2180	·1995	129 0	12900	1·2
120	2·3938	·2214	·1975	100 0	10100	0·9
130	2·3972	·2249	·1947	79·4	8160	0·7
140	2·4021	·2288	·1905	62·7	6560	0·6
150	2·4082	·2328	·1851	50·5	5370	0·5
			Benzene. Tube B.			
140	·9153	·4070	·3926	63·60	6650	2·6
150	·9119	·4142	·3963	50·90	5420	2·1
160	·9086	·4215	·3999	42·10	4560	1·8
170	·9057	·4296	·4032	34·30	3790	1·4
180	·9031	·4385	·4061	27·90	3140	1·2
190	·9011	·4481	·4085	22·70	2620	1·0
200	·8997	·4585	·4102	18 65	2195	0·8
210	·8989	·4703	·4113	15·23	1842	0·6
220	·8989	·4838	·4117	12·47	1550	0 5
230	·9003	·4994	·4107	10·15	1303	0·4
240	·9038	·5176	·4075	8·21	1092	0·3
250	·9107	·5399	·4009	6·55	909	0·2
260	·9229	·5684	·3890	5·14	751	0·2
270	9494	·6076	·3629	3·88	606	0·2
275	·9727	·6341	·3397	3·30	538	0·1
279·65	1 0117	·6676	·3009	2·76	473	0·1

The molecular volumes of saturated vapour do not lend themselves to graphical representation; but the logarithms of those values, mapped against the temperature, give serviceable curves. These were accordingly drawn, and the smoothed values for each 10° read off. They are given in the following table :—

Molecular Volumes of Saturated Vapours from Curves.

Temp	Fluorbenzene.	Chlorobenzene.	Bromobenzene.	Iodobenzene	Benzene.
80°	33200	—	—	—	28600
90	25000	—	—	—	21800
100	19000	—	—	—	16600
110	14700	—	—	—	12900
120	11500	—	—	—	10200
130	9080	32900	—	—	8180
140	7250	26000	—	—	6630
150	5860	20800	—	—	5420
160	4810	16600	29800	—	4490
170	3970	13500	23900	—	3730
180	3290	11000	19400	—	3130
190	2740	9050	15800	33800	2615
200	2290	7480	13000	27800	2195
210	1928	6240	10800	22900	1850
220	1622	5230	8950	19000	1552
230	1361	4410	7530	15700	1302
240	1140	3740	6310	13100	1091
250	950	3170	5350	11000	910
260	781	2690	4570	9250	650
270	624	2280	3900	7810	705
280	471	1940	3300	6620	469

These values agree very well with those observed with the exception of the volumes of bromobenzene at temperatures above 250°. These were inaccurate, for reasons already stated (p. 128), and the curve above 250° was therefore extrapolated. The error at 280° amounts to 5·5 per cent.

The molecular volumes of the saturated vapours at the boiling points of the substances under "corresponding" pressures (which, for the halogen derivatives, are equal pressures) were then read from the curves, and are given in the following table :—

Pressures.		Temperatures.					Molecular volumes of saturated vapour.				
Halogen derivatives	Benzene.	C_6H_5F.	C_6H_5Cl.	C_6H_5Br.	C_6H_5I.	C_6H_6.	C_6H_5F.	C_6H_5Cl.	C_6H_5Br.	C_6H_5I.	C_6H_6.
1000	1073	94·3	142·4	167·05	200·5	91 95	22300	24600	25500	27500	20500
1500	1610	109·0	159·2	184·8	219·45	106·85	15100	17000	17500	19200	13900
2000	2146	120·25	172 0	198·3	234 0	118 3	11400	13030	13150	14600	10560
3000	3220	137·4	191·6	219·0	256 0	135 9	7670	8760	9150	9910	7230
4000	4293	150 8	206·9	234·95	272·65	149 5	5750	6600	6910	7460	5480
5000	5366	161·85	219·45	248·35	—	160·75	4630	5250	5530	—	4420
6000	6439	171·25	230·0	259·1	—	170·5	3870	4410	4630	—	3690
8000	8586	187·4	247 95	277·9	—	183·8	2870	3280	3450	—	2770
10000	10732	200·6	262 35	—	—	200·3	2265	2575	—	—	2185
12000	12879	211·95	274·75	—	—	212·0	1862	2106	—	—	1782
15000	16098	226 7	—	—	—	227·05	1447	—	—	—	1371
20000	21464	246·7	—	—	—	247·5	1009	—	—	—	953
25000	26831	263·0	—	—	—	264·1	733	—	—	—	689
30000	32197	277·0	—	—	—	278 6	516	—	—	—	489
33912	36395	286·55	—	—	—	288·5	233*	—	—	—	219*

* From previous results with the liquids; direct readings.

The ratios of the molecular volumes at corresponding pressures are given in the table below.

Ratios of Molecular Volumes of Saturated Vapours at Corresponding Pressures.

Pressures.		Ratios.						
Halogen derivatives.	Benzene.	$\frac{C_6H_5Cl}{C_6H_5F}$.	$\frac{C_6H_5Br}{C_6H_5F}$.	$\frac{C_6H_5I}{C_6H_5F}$.	$\frac{C_6H_5Br}{C_6H_5Cl}$.	$\frac{C_6H_5I}{C_6H_5Cl}$.	$\frac{C_6H_5I}{C_6H_5Br}$.	$\frac{C_6H_6}{C_6H_5F}$.
1000	1073	1·105	1·145	1·235	1·035	1·120	1·080	0·925
1500	1610	1·125	1·160	1·270	1·035	1·130	1·095	0·925
2000	2146	1·135	1·180	1·280	1·040	1·130	1·090	0·930
3000	3220	1·145	1·195	1·295	1·045	1·130	1·085	0·945
4000	4293	1·145	1·200	1·295	1·045	1·130	1·080	0·955
5000	5366	1·140	1·195	—	1·045	—	—	0·955
6000	6439	1·140	1·195	—	1·050	—	—	0·955
8000	8586	1·145	1·205	—	1·050	—	—	0·965
10000	10732	1·140	—	—	—	—	—	0·965
12000	12879	1·130	—	—	—	—	—	0·955
15000	16098	—	—	—	—	—	—	0·945
20000	21464	—	—	—	—	—	—	0·945
25000	26831	—	—	—	—	—	—	0·940
30000	32197	—	—	—	—	—	—	0·945
33912	36395	—	—	—	—	—	—	0·940
Mean ratios ..		1·140	1·195	1·290	1·046	1·130	1·085	0·949

With the exception of the comparisons at the lowest pressures, it is evident that the molecular volumes of the saturated vapours bear an approximately constant ratio to each other at all corresponding pressures. In calculating the mean ratios, the results at 1000 and 1500 mm. have been omitted on account of the relatively large errors involved in their determinations.

It has been already pointed out that if Van der Waals' generalisations were strictly true, the following relation should hold good:—

$$\frac{V}{V'} = \frac{v}{v'} = \frac{T}{T'} \cdot \frac{p'}{p}.$$

Or in the case of the halogen derivatives of benzene, the critical pressures of which are equal, the simpler relation

$$\frac{V}{V'} = \frac{v}{v'} = \frac{T}{T'}.$$

In the following table, the mean ratios of the observed molecular volumes, both of the liquids V/V' and of the saturated vapours v/v', are compared with those calculated from the above formulæ. In the case of the halogen derivatives, the ratios T/T' are the mean ratios of the boiling points (on the absolute scale) at equal pressures. For benzene and fluorbenzene, the absolute critical temperatures are taken.

Substances compared.	$\frac{T}{T'}$.	$\frac{T}{T'} \cdot \frac{p'}{p}$.	Mean ratios of molecular volumes at corresponding pressures.	
			Liquids.	Saturated vapours.
C_6H_5Cl/C_6H_5F	1·1308	—	1·1244	1·140
C_6H_5Br/C_6H_5F	1·1974	—	1·1800	1·195
C_6H_5I/C_6H_5F............	1·2881	—	1·2772	1·290
C_6H_5Br/C_6H_5Cl...... .	1·0589	—	1·0494	1·046
C_6H_5I/C_6H_5Cl...........	1·1394	—	1·1359	1·130
C_6H_5I/C_6H_5Br	1·0760	—	1·0824	1·085
C_6H_6/C_6H_5F.............	—	0·9351	0·9435	0·919

It will be seen that the three ratios are in each case approximately equal, the greatest differences being between the ratios of the molecular volumes of liquid and saturated vapour in the first comparison, and between the ratio of the molecular volumes of the saturated vapour and the value $T/T' \times p'/p$ in the last. Both these differences are, however, under 1·5 per cent.

In conclusion, it may be pointed out that—assuming the truth of Van der Waals' generalisations—the ratio of the actual density of the saturated vapour to the theoretical density ($\frac{1}{2}$ molecular weight) should be the same for all stable substances at their boiling points under corresponding pressures.

For the vapour density of a substance is the ratio of its weight to that of the same volume of hydrogen at the same temperature and pressure; and if for any saturated vapour the volume taken (in c.c.) is the molecular volume (v), then the weight of substance will be its molecular weight M (in grams). Calling the boiling point on the absolute scale T and the pressure p, we have

$$\text{Density of saturated vapour} = \frac{M}{0{\cdot}0000896 \times v \times \frac{273}{T} \times \frac{p}{760}},$$

and since the theoretical vapour density = M/2, the ratio of the actual to the theoretical vapour density will be

$$R = \frac{2 \times 760}{0{\cdot}0000896 \times 273} \times \frac{T}{vp} = c\,\frac{T}{vp}.$$

Pressures.		Densities of saturated vapours (H = 1 at same temperature and pressure).					Ratio of actual to theoretical vapour density at corresponding pressures.				
Halogen derivatives.	Benzene.	C_6H_5F.	C_6H_5Cl.	C_6H_5Br.	C_6H_5I.	C_6H_6.	C_6H_5F.	C_6H_5Cl.	C_6H_5Br.	C_6H_5I.	C_6H_6.
1000	1073	49·12	58·86	84·07	108·6	40·06	1·025	1·049	1·074	1·068	1·029
1500	1610	50·20	59·21	84·77	108·3	40·96	1·048	1·056	1·083	1·065	1·052
2000	2146	51·33	60·00	85·39	109·7	41·68	1·072	1·070	1·091	1·079	1·071
3000	3220	53·13	61·63	87·19	112·5	42·49	1·109	1·099	1·114	1·106	1·092
4000	4293	54·80	63·38	89·41	115·5	43·41	1·144	1·130	1·142	1 136	1·115
5000	5366	55·86	65·05	91·74	—	44·25	1·166	1·159	1·172	—	1·137
6000	6439	56·88	66·26	93·21	—	45·09	1·188	1·181	1·190	—	1·159
8000	8586	59·74	69·19	97·08	—	46·70	1·247	1·233	1·240	—	1·200
10000	10732	62·25	72·44	—	—	48·81	1·300	1·291	—	—	1·254
12000	12879	64·60	75·55	—	—	51·10	1·349	1·347	—	—	1·313
15000	16098	68·52	—	—	—	54·80	1·431	—	—	—	1·408
20000	21464	76·64	—	—	—	61·55	1·600	—	—	—	1·582
25000	26831	87·08	—	—	—	70·30	1·818	—	—	—	1·806
30000	32197	105·70	—	—	—	84·84	2·206	—	—	—	2·180
33912	36395	210·60	—	—	—	170·2	4·397	—	—	—	4·374

For any other substance at its boiling point under the corresponding pressure p', the ratio of the actual to the theoretical vapour density is $R' = c \frac{T'}{v'p'}$.

But it has been already shown that for any two substances at corresponding pressures p and p'

$$\frac{v}{v'} = \frac{T}{T'} \cdot \frac{p'}{p}, \quad \text{or} \quad \frac{T}{vp} = \frac{T'}{v'p'}; \quad \text{therefore } R = R'.$$

As this is a very convenient method of comparing the saturated vapours of different substances, I have calculated the densities of the saturated vapours at the "corresponding" pressures which have already served as the basis of comparison, and also the ratios to the theoretical vapour densities.

The results are given in the table (p. 138) :—

At pressures above 1500 mm. there is a remarkably close agreement between the four halogen derivatives : the larger differences in the ratios at the lowest pressures may be due, in part at any rate, to errors of experiment. With regard to benzene and fluorbenzene, the general agreement throughout, even including the direct observations at the critical points, is very striking; the differences, however, which reach a maximum of nearly 4 per cent. at a pressure of 8000 mm., cannot be explained by experimental errors, and are certainly real.

The results obtained may be summarised as follow :—

1. The molecular volumes of the saturated vapours of benzene and its halogen derivatives bear an approximately constant ratio to each other at all "corresponding" pressures.

2. The molecular volumes of the saturated vapours of these substances at their boiling points under "corresponding" pressures are, approximately, directly proportional to their absolute critical temperatures, and inversely proportional to their critical pressures.

3. The ratios of the actual densities of the saturated vapours (compared with hydrogen at the same temperature and pressure) to the normal vapour densities (½ molecular weight) are approximately equal for these substances at their boiling points under "corresponding" pressures.

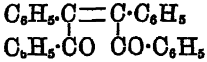
4. The critical pressures of the halogen derivatives being equal, "corresponding" pressures are equal pressures. For these substances the deviations from constancy are small, and may be due to errors of experiment. In the comparisons of benzene with fluorbenzene, however, the deviations, though not very great, are certainly not entirely due to experimental error.

The first two relations have already been found to hold for the molecular volumes of the liquids.

XVI.—*The Action of Ammonia and of Methylamine on the Oxylepidens.*

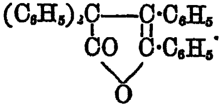
By FELIX KLINGEMANN, Ph.D., and W. F. LAYCOCK, Ph.D.

THE constitution of the so-called oxylepidens discovered by Zinin has been settled of late by the researches of Magnanini and Angeli (*Ber.*, **22**, 853), and of Japp and Klingemann (Trans., 1890, 665), Magnanini and Angeli have found that "acicular oxylepiden" has the constitution



$\begin{matrix} C_6H_5\cdot C & = & C\cdot C_6H_5 \\ C_6H_5\cdot CO & & CO\cdot C_6H_5 \end{matrix}$

; and it may, therefore, be called dibenzoylstilbene. It is changed by heating into "tabular oxylepiden," which, according to Japp and Klingemann, is to be regarded as tetraphenylcrotolactone,



. We shall, in this paper, employ, in place of Zinin's provisional names, "acicular oxylepiden" and "tabular oxylepiden," the systematic appellations *dibenzoylstilbene* and *tetraphenylcrotolactone.*

PART I.—THEORETICAL.

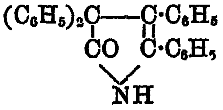
Japp and Klingemann have pointed out the striking analogy between $\alpha\beta$-dibenzoylcinnamene and dibenzoylstilbene. Both compounds are changed into anhydrides of γ-ketonic acids by heating, the former yielding triphenylcrotolactone, the latter tetraphenylcrotolactone. By the action of alcoholic ammonia on $\alpha\beta$-dibenzoylcinnamene, the same authors obtained a compound of the formula $C_{22}H_{17}NO$, which on heating is changed into an isomeride As the latter is also produced by the action of alcoholic ammonia on triphenylcrotolactone, in this case without the formation of any intermediate product, they assigned to it the constitution of a lactam of benzoyldiphenylpropionic acid. Methylamine acts in a slightly different way; with $\alpha\beta$-dibenzoylcinnamene, it yields, at once, the methylated lactam of benzoyldiphenylpropionic acid, whilst with triphenylcrotolactone, it forms at first an additive compound, the methylamide of the same acid, which on heating parts with the elements of water and yields the methylated lactam.

In order to show that the great analogy existing between $\alpha\beta$-dibenzoylcinnamene and dibenzoylstilbene also holds good in their behaviour towards ammonia and primary amines, we have made experiments with this object and have found that in this case also the parallelism of the reactions of the two unsaturated γ-diketones is nearly complete.

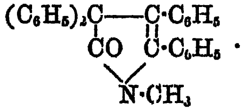
By the action of alcoholic ammonia on dibenzoylstilbene, two compounds are obtained of the formula $C_{28}H_{21}NO$, melting at 180—182° and at 206—207° respectively. The one of lower melting point is changed by heating into the higher melting modification, and the latter is also obtained by the action of alcoholic ammonia on tetraphenylcrotolactone.

Methylamine reacts with dibenzoylstilbene with elimination of water, forming the methyl-substituted lactam of benzoyltriphenylpropionic acid. Tetraphenylcrotolactone unites directly with methylamine, yielding the methylamide of benzoyltriphenylpropionic acid. This methylamide, when distilled in a vacuum, parts with water, and yields the methylated lactam of benzoyltriphenylpropionic acid. The two preparations of this lactam obtained by these processes show slight differences in melting point and solubility; their crystallographical properties also seem quite different. We do not, however, regard them as chemically different compounds, but only as dimorphic modifications of the same compound; we have the more reason to suppose this view to be correct as the alkyl-substituted lactams of benzoyldiphenylpropionic acid also very frequently exhibit polymorphism.

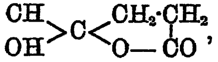
As regards the constitution of these compounds, we think it most probable that the ammonia derivative melting at 206—207° and the methylated lactam are to be regarded as corresponding compounds, the constitution of which may be represented by the formulæ

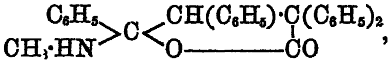

Ammonia derivative
(m. p. 206—207°).

and


Methylamine derivative
(m. p. 158° *and* 161°).

We adopt for these compounds the same nomenclature as that used by Japp and Klingemann for the corresponding derivatives of triphenylcrotolactone. Thus the ammonia derivative would be 3-*diphenyl-4* : 5-*phenylpyrrholone* and the methylamine derivative 1-*methyl-3-diphenyl-4* : 5-*phenylpyrrholone.*

The additive compound of tetraphenylcrotolactone and methylamine is to be regarded as the methylamide of benzoyltriphenylpropionic acid. The constitution of γ-ketonic acids has lately been the subject of much discussion. Whilst they are generally believed to be true acids, Bredt has suggested (*Annalen,* **256**, 314) that in many cases they react as if they had the constitution of γ-hydroxylactones. In the case of lævulinic acid, he has shown that the chloride, the cyanide, and the acetyl compound of this acid react with phenylhydrazine with elimination of hydrogen chloride, hydrogen cyanide, and acetic acid respectively, forming the hydrazide of phenylhydrazonelævulinic acid. This leads him to consider these three compounds as derivatives of the γ-hydroxylactone  $\begin{matrix}CH\\OH\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\cdot\overset{}{C}H_2\\ \vert\\ O—CO\end{matrix}$, in which the hydroxyl group is replaced by the acid radical. Should Bredt's view be correct our methylamide would have the constitution—



$$\begin{matrix}C_6H_5\\CH_3\cdot HN\end{matrix}\!>\!C\!<\!\begin{matrix}CH(C_6H_5)\cdot C(C_6H_5)_2\\ \vert\\ O\text{————————}CO\end{matrix},$$

whilst if we regard γ-ketonic acids as true acids, the constitution of the same compound would be expressed by the formula

$$C_6H_5\cdot CO\cdot CH(C_6H_5)\cdot C(C_6H_5)_2\cdot CO\cdot NH\cdot CH_3.$$

The last formula seems to express better the property the compound has of yielding methyltetraphenylpyrrholone with elimination of water when subjected to a high temperature.

Part II.—Experimental.

Action of Alcoholic Ammonia on Dibenzoylstilbene.

Dibenzoylstilbene was heated in a sealed tube with a large excess of alcoholic ammonia at 200° for five hours. On standing, the solution deposited small, square plates, and the addition of water to the mother liquor from these produced a voluminous yellow precipitate. The plates were recrystallised several times from alcohol; after the second recrystallisation, they melted constantly at 206—207°, and were of a pale-yellow colour; 4 grams of the crystals were obtained from 20 grams of dibenzoylstilbene. Analysis showed that the compound has the formula $C_{28}H_{21}NO$. Its formation is expressed by the equation

$$C_{28}H_{20}O_2 + NH_3 = C_{28}H_{21}NO + H_2O.$$

I. 0·2187 gram substance gave 0·6971 gram CO_2 and 0·1087 gram H_2O.

II. 0·1178 gram substance gave 9·02 c.c. dry N at 17° and 298 mm.

	Calculated for $C_{28}H_{21}NO$.		Found.	
			I.	II.
C_{28}	336	86·82	86·92	—
H_{21}	21	5·43	5·52	—
N	14	3·62	—	3·55
O	16	4·13	—	—
	387	100·00		

The yellow precipitate from the mother liquors was dried on filter paper and was divided by fractional crystallisation from benzene into two portions melting at 185—190° and at 178—180° respectively. The former consisted mainly of the substance described above crystallising in plates; the latter was purified by repeated recrystallisation from a mixture of benzene and light petroleum, and finally from benzene alone. The pure substance separates from this solvent in hard crusts of yellow, prismatic crystals melting at 180—182°. Analysis shows it to be an isomeride of the substance described above.

I. 0·1475 gram substance gave 0·4707 gram CO_2 and 0·0738 gram H_2O.

II. 0·1798 gram substance gave 0·5725 gram CO_2 and 0·0905 gram H_2O.

III. 0·1352 gram substance gave { dry N + NO 9·02 c.c. at 19° and 407 mm,
dry N 902 c.c. at 19·5° and 390 mm.

	Calculated for $C_{28}H_{21}NO$.		Found.		
			I.	II.	III.
C_{28}	336	86·82	87·03	86·83	—
H_{21}	21	5·43	5·55	5·59	—
N	14	3·62	- -	—	4·10
O	16	4·13	—	—	—
	387	100·00			

By heating this substance to 310°, it is changed into the modification of higher melting point; we heated a specimen of the pure substance in a bath of diphenylamine vapour for about ten minutes, and recrystallised the fused substance from alcohol; it separated in square plates melting at 206°. In spite of the rather deep yellow colour of the compound, we analysed it, as the small amount at our disposal rendered further purification impossible.

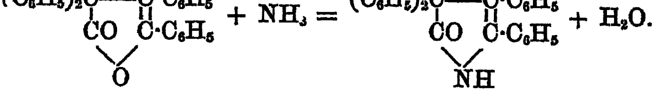
I. 0·1123 gram substance gave 0·3597 gram CO_2 and 0·0577 gram H_2O.

II. 0·0998 gram substance gave
- dry N + NO 9·02 c.c. at 21° and 291 mm.
- dry N 9·02 c.c. at 21° and 274 mm.

	Calculated for $C_{28}H_{21}NO$.		Found. I.	Found. II.
C_{28}	336	86·82	87·35	—
H_{21}..........	21	5·43	5·70	—
N	14	3·62	—	3·91
O	16	4·13	—	—
	387	100·00		

This compound corresponds with dibenzoylcinnamenimide, obtained by Japp and Klingemann by mixing the alcoholic solutions of ammonia and dibenzoylcinnamene. It is converted by heating into the lactam of benzoyldiphenylpropionic acid (triphenylpyrrholone). In the same way our compound, which we will call dibenzoylstilbenimide, on heating yields the lactam of benzoyltriphenylpropionic acid (tetraphenylpyrrholone). That the compound melting at 207° has really the constitution of tetraphenylpyrrholone is shown by the following reaction.

Action of Alcoholic Ammonia on Tetraphenylcrotolactone.—Tetraphenylcrotolactone was heated with an excess of alcoholic ammonia for four hours at 200°. The solution on cooling deposited a substance crystallising in square plates. After repeated crystallisation from alcohol, the melting point became constant at 206—207°. This substance was identical in every respect with the higher melting substance obtained from alcoholic ammonia and dibenzoylstilbene. It has the formula $C_{28}N_{21}NO$, and is therefore formed according to the equation



The systematic name would be 3-*diphenyl-4 : 5-phenylpyrrholone.* The yield is very satisfactory. On anaylsis, it gave the following results :—

I. 0·1444 gram substance gave 0·4611 gram CO_2 and 0·0707 gram H_2O.

II. 0·2505 gram substance gave 0 7968 gram CO_2 and 0·1166 gram H_2O.

III. 0·1113 gram substance gave
dry N + NO 9 02 c.c. at 19·5° and 270 mm.
dry N 9 02 c.c. at 19·5° and 266 mm.

IV. 0·1176 gram substance gave
dry N + NO 9·02 c.c. at 16° and 314 mm.
dry N 9·02 c.c. at 16° and 290 mm.

	Calculated for $C_{28}H_{21}NO$.		Found.			
			I.	II.	III.	IV.
C_{28}	336	86·82	87·08	86·74	—	—
H_{21}	21	5·43	5·44	5·17	—	—
N	14	3·62	—	—	3·34	3·61
O	16	4 13	—	—	—	—
	387	100 00				

Reduction of Tetraphenylpyrrholone.—3·8 grams of the compound were dissolved in boiling amyl alcohol and reduced with 4 grams of sodium. After agitating with water to remove the alkali, the amyl alcohol was boiled off, at first at the ordinary pressure, then in a vacuum on the water-bath. The brown, crystalline residue was recrystallised thrice from alcohol, and was thus obtained in the form of slender, light-brown needles, melting at 237°. Analysis showed the compound to have the formula $C_{28}H_{23}NO$.

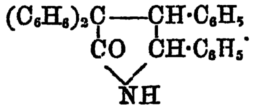
I. 0·1860 gram substance gave 0·5870 gram CO_2 and 0·1004 gram H_2O.

II. 0·1611 gram substance gave 0·5092 gram CO_2 and 0·0868 gram H_2O.

III. 0·1177 gram substance gave
dry N + NO 9·02 c.c. at 19 5° and 300 mm.
dry N 9·02 c.c. at 19·5° and 286 mm.

	Calculated for $C_{28}H_{23}NO$.		Found.		
			I.	II.	III.
C_{28}	336	86·38	86·07	85·93	—
H_{23}	23	5·91	5·99	5·96	—
N	14	3·60	—	—	3·46
O	16	4·11	—	—	—
	389	100 00			

This compound is formed, therefore, from tetraphenylpyrrholone by the addition of 2 atoms of hydrogen. It is to be regarded as a 3-*diphenyl*-4 : 5-*phenylpyrrholidone*, having the constitution



Action of Methylamine on Dibenzoylstilbene.

Six grams of dibenzoylstilbene were heated in a sealed tube with an excess of alcoholic methylamine for two hours to 200°. From the concentrated solution, a yellow, crystalline compound separated on standing. This was recrystallised from alcohol, and separated from the concentrated solution in tufts of light-brown needles melting at 157°. The yield was good, 4·3 grams of recrystallised substance being obtained, and 1 gram of less pure substance from the mother liquors. As this specimen did not give sufficiently sharp figures on analysis, it was once more recrystallised first from a mixture of benzene and light petroleum, from which it separated in yellow nodules, and then from boiling alcohol, from which it crystallised in small, thin plates of an asymmetrical shape; the colour was a very pale yellow, and it melted at 161°. Analysis showed that the compound had the formula $C_{29}H_{23}NO$. It had consequently been formed according to the equation

$$C_{28}H_{20}O_2 + NH_2{\cdot}CH_3 = C_{29}H_{23}NO + H_2O.$$

I. 0·2194 gram substance gave 0·6956 gram CO_2 and 0·1127 gram H_2O.

II. 0·1297 gram substance gave $\left\{\begin{array}{l}\text{dry N + NO 9·02 c.c. at 22·5° and 358 mm.}\\ \text{dry N 9·02 c.c. at 22·5° and 350 mm.}\end{array}\right.$

	Calculated for $C_{29}H_{23}NO$.		Found.	
			I.	II.
C_{29}..........	348	86·78	86·46	—
H_{23}..........	23	5·74	5·70	—
N..........	14	3·49	—	3·76
O..........	16	3·99	—	—
	401	100·00		

It is fairly soluble in boiling alcohol, extremely so in cold benzene, and readily in carbon bisulphide; from the last solvent, it separates in yellow, well-shaped, tabular crystals.

Action of Methylamine on Tetraphenylcrotolactone.

12·5 grams of tetraphenylcrotolactone were heated with an excess of alcoholic methylamine for one hour at 100°. A crystallised product was obtained. This was extracted with boiling alcohol, which dissolved the greater part of it, leaving 3·5 grams of a sparingly soluble compound undissolved. The alcoholic solution deposited 7 grams of a crystallised product, which was again treated with alcohol. 6·7 grams of the sparingly soluble compound was left, the rest separating from the filtered solution in plates melting at 134°.* This soluble compound was therefore only unchanged tetraphenylcrotolactone. The sparingly soluble compound was recrystallised from boiling glacial acetic acid, from which it separated in small, lustrous plates of a triclinic shape melting at 260°; by repeated recrystallisation, the melting point was raised to 267°. In a second experiment also, we found that a great part of the tetraphenylcrotolactone was left unchanged, although a fair excess of methylamine had been used, and the reaction had been carried on at 150°. Analysis gave figures agreeing with the formula of an additive compound of methylamine and tetraphenylcrotolactone.

I. 0·2285 gram substance gave 0·6924 gram CO_2 and 0·1214 gram H_2O.

II. 0·2044 gram substance gave 0·6222 gram CO_2 and 0·1105 gram H_2O.

III. 0·1435 gram substance gave { dry N + NO 9·02 c.c. at 22° and 367 mm. / dry N 9·02 c.c. at 22° and 334 mm.

	Calculated for $C_{29}H_{25}NO_2$.		Found.		
			I.	II	III.
C_{29}	348	83·05	82·63	83·02	—
H_{25}	25	5·97	5·90	6·00	—
N	14	3·34	—	—	3·36
O_2	32	7·64	—	—	—
	419	100·00			

We regard this compound as the methylamide of benzoyltriphenylpropionic acid, having probably the constitution

$$C_6H_5\cdot CO\cdot CH(C_6H_5)\cdot C(C_6H_5)_2\cdot CO\cdot NH\cdot CH_3.$$

---

* A qualitative test showed the absence of nitrogen.

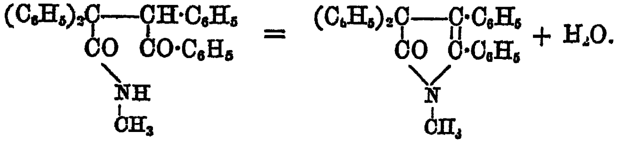
In a perfectly analogous manner, triphenylcrotolactone and methylamine yield the methylamide of benzoyldiphenylpropionic acid. The physical properties of the two compounds are, however, remarkably different; whilst the latter is a compound of a comparatively low melting point (156°) and readily soluble in most solvents, our new methylamide is distinguished by its high melting point (267°), and by being very sparingly soluble in boiling alcohol and even in acetic acid.

Distillation of Benzoyl Triphenylpropiomethylamide.

This compound is much more stable under the influence of heat than the corresponding derivative of triphenylcrotolactone. Even when heated for several minutes in a bath of diphenylamine vapour, it is quite unchanged. A specimen treated in this way gave on analysis the following figures:—

Calculated for $C_{29}H_{25}NO_2$, C....	83·05	H....	5·97
Found, C....................	82·90	H....	6·31

To decompose it, it was found necessary to distil it in an Anschütz flask on a graphite-bath under diminished pressure. The distillate consisted of water and a solid red substance; the latter was dissolved in alcohol, and as the compound did not separate spontaneously the crystallisation was started by rubbing the sides of the beaker with a glass rod. It then crystallised out in transparent, pale yellow nodules melting at 158°. The composition of the compound is expressed by the formula $C_{29}H_{23}NO$. Its formation may be represented by the equation



I. 0·1437 gram substance gave 0·4565 gram CO_2 and 0·0734 gram H_2O.

II. 0·1638 gram substance gave 0·5176 gram CO_2 and 0·0836 gram H_2O.

III. 0·1371 gram substance gave { dry N + NO 9·02 c.c. at 20° and 336 mm.
dry N 9·02 c.c. at 20° and 319 mm.

	Calculated for $C_{29}H_{23}NO$.		Found.		
			I.	II.	III.
C_{29}	348	86·78	86·63	86·18	—
H_{23}	23	5·74	5·67	5·67	—
N	14	3·49	—	—	3·31
O	16	3·99	—	—	—
	401	100·00			

This compound would, therefore, be called 1-*methyl*-3-*diphenyl*-4 : 5-*phenylpyrroholone.*

In order to compare it with the compound $C_{29}H_{23}NO$ obtained from dibenzoylstilbene and methylamine, which we consider to have the same constitution, it was recrystallised first from benzene, from which it separates in long, prismatic crystals, and then from carbon bisulphide; it is by no means readily soluble in the latter, and separates from it in long needles melting at 158°. Mr. Tutton had the kindness to examine the crystallographical properties of both preparations, and although, owing to the striation of the faces, he could not obtain very satisfactory results, his examination also tends to show that they are different. The compound melting at 161° appears to be rhombic, the tabular crystals showing the rings in the centre well. The compound melting at 158° appears to consist of monoclinic prisms. At any rate, the habit and the faces are quite different from those of the compound melting at 161°. However, as we have already pointed out in the theoretical part of this paper, we believe that both forms have the same constitution, and that they are only dimorphic modifications of the same compound. We also tried to convert the higher melting modification into that of lower melting point by distilling it in a vacuum, but owing to the very small amount at our disposal we could not carry out this reaction successfully.

The reaction between dibenzoylstilbene and phenylhydrazine has been studied by one of us, and will be published in a short time Also the investigation of benzoylphenylpropionic acid (desylacetic acid) has been taken up, and the lactam of this acid (diphenylpyrrholone) and other derivatives have been prepared.

We are very much indebted to Dr. Japp for several valuable suggestions, and take this opportunity of thanking him for his assistance.

XVII.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

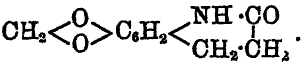
Some Derivatives of Piperonyl.

By FREDERICK M. PERKIN.

DURING an investigation on the constitution of berberine, which was undertaken by my brother (Trans., 1890, **57**, 992), a compound, $C_{10}H_9NO_3$, was obtained, the determination of the constitution of which was of the utmost importance in assigning the correct formula to the alkaloïd.

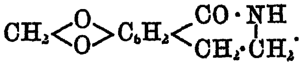
A careful examination of the substance showed that it was the anhydride of an amidoethylpiperonylcarboxylic acid, but for a long time no proof of the exact position of the atoms in the side chains could be obtained, and both the following formulæ equally well accounted for the reactions of the substance:—

I.



$$CH_2<\substack{O\\O}>C_6H_2<\substack{NH\cdot CO\\CH_2\cdot CH_2}.$$

II.



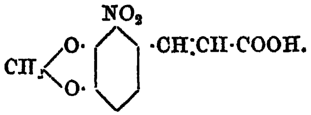
$$CH_2<\substack{O\\O}>C_6H_2<\substack{CO\cdot NH\\CH_2\cdot CH_2}.$$

Several methods were employed in order to discriminate between these two, before it was ultimately shown that formula II was the correct expression of the constitution of the compound, and, amongst others, a number of experiments were made with the object of preparing this substance synthetically from piperonal. A short account of these I beg now to lay before the Society.

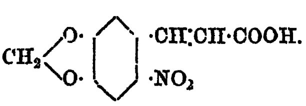
Lorenz (*Ber.*, **13**, 757) has shown that piperonal, when digested with sodium acetate and acetic anhydride, is readily converted into piperonylacrylic acid, $CH_2<\substack{O\\O}>C_6H_3\cdot CH{:}CH\cdot COOH$. This acid was, I found, readily acted on by nitric acid, yielding a mononitro-acid, $CH_2<\substack{O\\O}>C_6H_2(NO_2)\cdot CH{:}CH\cdot COOH$.

On treating nitropiperonal with acetic anhydride and sodium acetate, I obtained an acid which was identical with that obtained by the nitration of piperonylacrylic acid, and as Liebermann and Faber (*Ber.*, **23**, 1566) have lately shown that the nitro-group in nitropiperonal is in the ortho-position to the aldehyde group, it therefore follows that the nitro-acid from piperonylacrylic acid must contain the nitro-group in the ortho-position to the acrylic acid group, and that the acid has, therefore, one of the two following formulæ:—

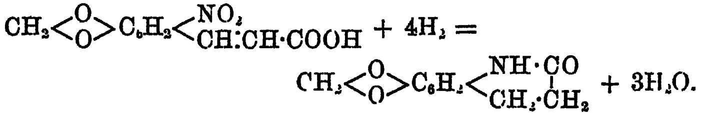
I.



II.



The nitro-acid, on reduction with ferrous hydrate, yields the corresponding amido-acid, $CH_2<\substack{O\\O}>C_6H_2<\substack{NH_2\\CH:CH\cdot COOH}$, but reduction with zinc or tin and hydrochloric acid converts the nitro-acid into ethylamidopiperonyl-α-carboxylic anhydride, $C_{10}H_9NO_3$, thus:—

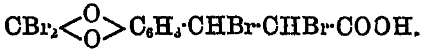


$$CH_2<\substack{O\\O}>C_6H_2<\substack{NO_2\\CH:CH\cdot COOH} + 4H_2 = CH_2<\substack{O\\O}>C_6H_2<\substack{NH\cdot CO\\ \vert \\ CH_2\cdot CH_2} + 3H_2O.$$

This interesting substance is isomeric with α-amidoethylpiperonylcarboxylic anhydride obtained from berberine; the former is a derivative of quinoline, the latter is the corresponding isoquinoline derivative.

In addition to these experiments, the behaviour of piperonylacrylic acid with bromine was carefully investigated.

When submitted to the action of bromine vapour, this acid readily takes up 4 atoms of bromine, with evolution of hydrogen bromide, yielding a tetrabromo-acid, which very probably has the formula

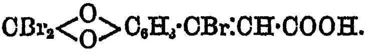


$$CBr_2<\substack{O\\O}>C_6H_3\cdot CHBr\cdot CHBr\cdot COOH.$$

This tetrabromo-acid is readily decomposed by boiling with alcoholic potash, with formation of a variety of products which could be separated only with great difficulty. Four products were ultimately isolated, but two of these could not be obtained in a state of perfect purity.

These products appear, however, to have the following formulæ:—

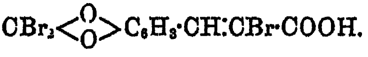
I.



$$CBr_2<\substack{O\\O}>C_6H_3\cdot CBr:CH\cdot COOH.$$

β-Tribromopiperonylacrylic acid,

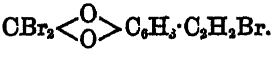
II.



$$CBr_2<\substack{O\\O}>C_6H_3\cdot CH:CBr\cdot COOH.$$

α-Tribromopiperonylacrylic acid.

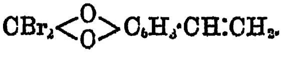
III.



$$CBr_2<\substack{O\\O}>C_6H_3\cdot C_2H_2Br.$$

Tribromopiperonylethylene.

IV.



$$CBr_2<\substack{O\\O}>C_6H_3\cdot CH:CH_2.$$

Dibromopiperonylethylene.

The formation of these substances will be readily understood from the following equations:—

$$\text{I. } \mathrm{CBr_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}COOH} + \mathrm{3KOH} =$$
$$\mathrm{CBr_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}C_2H_2Br} + \mathrm{KBr} + \mathrm{K_2CO_3} + \mathrm{2H_2O}.$$

$$\text{II. } \mathrm{2CBr_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}COOH} + \mathrm{4KOH}$$
$$= \mathrm{CBr_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CBr{:}CH{\cdot}COOK} +$$
$$\mathrm{CBr_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CH{:}CBr{\cdot}COOK} + \mathrm{2KBr} + \mathrm{4H_2O}.$$

In the formation of the substance represented by formula I, it is obvious that the alcoholic potash employed in the reaction must have acted as a reducing agent, thus:—

$$\mathrm{CBr_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}COOH} + \mathrm{4KOH} + \mathrm{H_2}$$
$$= \mathrm{CBr_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CH{:}CH_2} + \mathrm{2KBr} + \mathrm{K_2CO_3} + \mathrm{3H_2O}.$$

Experiments on the action of potassium cyanide on piperonal were also instituted, and the result showed that a substance was formed which proved to be related to piperonal exactly as benzoin is to benzaldehyde. This compound, for which I propose the name of piperonyloin, is formed according to the equation

$$\mathrm{2CH_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}COH} = \mathrm{CH_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CO{\cdot}CH(OH){\cdot}C_6H_3}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{CH_2}.$$

When warmed with nitric acid, it is very readily oxidised, but as yet the corresponding diketone has not been isolated. Experiments on this point are in progress.

Piperonylacrylic Acid, $\mathrm{CH_2}{<}\substack{\mathrm{O}\\ \mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CH{:}CH{\cdot}COOH}$.

This acid was first obtained by Lorenz (*Ber.*, **13**, 757). In preparing considerable quantities of it, I have found the following method to give good results.

20 grams of piperonal, 24 grams of acetic anhydride, and 14 grams of fused sodium acetate are heated in a paraffin-bath to gentle boiling for 7 hours using a reflux condenser. The product, which solidifies completely on cooling, was melted and poured into cold water, boiled with excess of dilute potassium hydrate, and the cold solution of the potassium salt freed from a quantity of an oily substance by extracting twice with ether. The alkaline solution, on the addition of hydrochloric acid, deposited a greyish precipitate; this was collected,

washed with water, dried, and recrystallised from glacial acetic acid.

In this way, the acid was readily obtained pure in the form of small, almost colourless needles. The analysis gave the following numbers, agreeing with the formula of piperonylacrylic acid:—

0·1847 gram of substance gave 0·4237 gram CO_2 and 0·0711 gram H_2O.

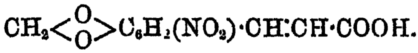
	Theory for $C_{10}H_8O_4$.	Found.
C	62·44 per cent.	62·55 per cent.
H	4·16 „	4·25 „

This acid exhibited the properties ascribed to it by Lorenz, with the exception that the sample prepared by me had a melting point of 238°, whereas Lorenz gives 232°.

The ethereal solution of the oil obtained as described above was evaporated and the residue distilled in a vacuum; a colourless oil then passed over, which solidified on cooling to a mass of crystals melting at 37°, and showed all the properties of piperonal.

Action of Nitric Acid on Piperonylacrylic Acid.

Nitropiperonylacrylic Acid,



$CH_2{<}^{O}_{O}{>}C_6H_2(NO_2)\cdot CH{:}CH\cdot COOH$.

In studying this interesting action, 2 grams of pure piperonylacrylic acid was ground up as finely as possible and added, in small quantities at a time, to 10 grams of nitric acid (sp. gr. 1·46), the whole being well cooled with ice and salt during the operation. At first, the acid appeared to dissolve, but, as the addition proceeded, it remained suspended in the liquid, the resulting product being a thin, yellow paste. This was thrown on to ice, the yellow, flocculent precipitate which separated collected, washed well with water, dried on a porous plate, and extracted once or twice with small quantities of boiling alcohol. In this way, a bye product present in the precipitate was readily separated from the mononitro-acid, the former being moderately soluble in boiling alcohol, whilst the mononitro-acid is sparingly soluble. The residual crude mononitro-acid was further purified by recrystallisation from boiling glacial acetic acid, from which it was deposited on cooling in brilliant, yellow plates. The analysis gave the following results:—

0·1223 gram substance gave 0·2256 gram CO_2 and 0·0360 gram H_2O.

0·2118 gram substance gave 11·4 c.c. nitrogen; $t = 16°$; bar. $= 756$ mm.

	Theory for $C_{10}H_7NO_6$.	Found.
C	50·63	50·30
H	2·95	3·27
N	5·90	6·24

When heated in a capillary tube, mononitropiperonylacrylic acid decomposes completely and becomes quite black at 240°, so that no definite melting point could be obtained. It is sparingly soluble in alcohol, benzene, and chloroform; almost insoluble in water, carbon bisulphide, and light petroleum. It dissolves readily in boiling acetic acid; and, on cooling, separates out again almost completely in the form of thin, yellow plates. The acid is also readily soluble in concentrated sulphuric acid, giving an orange-coloured solution; it is reprecipitated in yellow flocks on the addition of water.

Salts of Mononitropiperonylacrylic Acid.

Silver Salt, $C_{10}H_6NO_6Ag$.—In order to prepare this salt, about 2 grams of the pure acid was dissolved in a slight excess of ammonia and placed in a vacuum desiccator over sulphuric acid, until free from excess of ammonia; two or three drops of dilute nitrate of silver solution were added, the precipitate removed by filtration, and the filtrate precipitated by excess of nitrate of silver solution. The dirty-brown silver salt thus obtained was collected, well washed with water, dried at 100°, and analysed with the following result:—

I. 0·2421 gram substance gave 0·3110 gram CO_2 and 0·0435 gram H_2O.
0·1666 gram substance gave 0·0518 gram silver.
II. 0·2421 gram substance gave 0·0763 gram silver.

	Theory for $C_{10}H_6NO_6Ag$.	Found.	
		I.	II.
C	34·88	35·03	—
H	1·74	1·99	—
Ag	31·39	31·09	31·51

This silver salt appears to be slightly soluble in water; when rapidly heated, it deflagrates somewhat violently.

Sodium Salt, $C_{10}H_6NO_6Na$.—In preparing this salt, the pure acid was suspended in water, and dilute sodium hydrate solution added drop by drop, until all the acid had dissolved. The dark reddish-brown solution thus obtained was concentrated on a water-bath, and allowed to stand for some hours. The crystals which separated were collected, drained on a piece of porous plate, dissolved in a little water, and the solution digested with freshly-ignited animal charcoal and filtered. The solution, on standing, deposited the pure salt as a pale yellow, crystalline powder. The salt, on drying, at 100°, lost considerably in weight, and became opaque; it, therefore, contains water of crystallisation, the amount of which was not determined.

The analysis of the salt gave the following numbers:—

0·2800 gram substance, heated with sulphuric acid, gave 0·0776 gram Na_2SO_4.

	Theory for $C_{10}H_6NO_6Na$.	Found.
Na........	8·88 per cent.	8·98 per cent.

The sodium salt is readily soluble in water. The yellow solution shows the following behaviour with reagents.

Lead acetate, a yellowish-white, flocculent precipitate, almost insoluble in water.

Copper sulphate, a bright-green precipitate, very sparingly soluble in water.

Barium chloride gives a pale-yellow, crystalline precipitate, readily soluble in water; on cooling, it crystallises out in beautiful, deep-yellow, feathery needles.

Calcium chloride, a yellow, semi-crystalline precipitate, readily soluble in water, separating on cooling in well-formed, microscopic prisms.

During the preparation of nitropiperonylacrylic acid, a small quantity of a bye product is formed, which is readily separated from the nitro-acid by means of alcohol. The alcoholic extract, on evaporation, deposits the new substance in the form of fine, brown needles which, after repeated recrystallisation from alcohol, are readily obtained pure.

As this substance is extremely explosive, the greatest care had to be taken in conducting the analysis, it being necessary to mix it intimately with large quantities of powdered oxide of copper.

The following results were obtained on analysis:—

I. 0·2138 gram substance gave 0·2056 gram CO_2 and 0·0374 gram H_2O.
0·1962 gram substance gave 16 c.c. nitrogen; $t = 11°$; bar. $= 750$ mm.

II. 0·1098 gram substance gave 0·1077 gram CO_2 and 0·0241 gram H_2O

	Found.		
	I.	II.	
C...........	26·44	26·75	per cent.
H...........	1·94	2·43	„
N...	9·59	–	„

No clue has as yet been obtained to the constitution of this remarkable substance.

Methyl Nitropiperonylacrylate, $CH_2{<}^{O}_{O}{>}C_6H_2(NO_2)\cdot CH{:}CH\cdot COOCH_3$, and *Ethyl Nitropiperonylacrylate*, $CH_2{<}^{O}_{O}{>}C_6H_2(NO_2)\cdot CH{:}CH\cdot COOC_2H_5$.

In order to prepare the methyl salt of mononitropiperonylacrylic acid, the pure mononitro-acid was mixed with a considerable excess of methyl alcohol, the solution saturated with hydrogen chloride, and the product heated to boiling for an hour in a flask connected with a reflux apparatus. During this operation the greater part of the acid dissolved, giving a brownish solution; this was filtered from undissolved matter, allowed to cool, and the pale-yellow crystals which separated collected, washed with a little alcohol, spread on a porous plate, and recrystallised from alcohol. The needle-shaped crystals thus obtained gave the following numbers on analysis :—

0·1508 gram of substance gave 0·2914 gram CO_2 and 0·0553 gram H_2O.

	Theory for $C_{11}H_9NO_6$.	Found.
C	52·58 per cent.	52·67 per cent.
H	3·58 „	4·06 „

This salt crystallises from alcohol in fine, pale-yellow, silky needles which melt at 152°, and turn dirty brown on exposure to light. It is moderately soluble in hot alcohol, but is only very sparingly soluble in the cold, and is almost insoluble in water.

The *ethyl salt* was prepared in a similar manner to the methyl salt, substituting ethyl alcohol in place of methyl alcohol. It crystallises from alcohol in yellowish-brown needles which melt at 113—114°. The analysis gave the following numbers :—

0·1550 gram substance gave 0·3070 gram CO_2 and 0·0626 gram H_2O.

	Theory for $C_{12}H_{11}NO_6$.	Found.
C	54·34 per cent.	54·02 per cent.
H	4·15 „	4·48 „

Mononitropiperonylacrylic Acid from Nitropiperonal.

Nitropiperonal is readily prepared by acting on piperonal with nitric acid (sp. gr. 1·4), according to the method of Fittig and Remsen (*Annalen*, **159**, 134). A sample of this substance recrystallised from water gave the following numbers on analysis :—

0·1530 gram substance gave 0·2751 gram CO_2 and 0·0404 gram H_2O.

0·1440 gram substance gave 9 c.c. nitrogen; $t = 12·5°$; bar. = 760 mm.

	Theory for $C_8H_5NO_5$.	Found.
C	49·23 per cent.	49·03 per cent.
H	2·56 ,,	2·93 ,,
N	7·18 ,,	7 43 ,,

The extraordinary sensitiveness of this substance to light has been noticed by Fittig and Remsen (*Annalen*, **159**, 134), and by Liebermann and Haber (*Ber.*, **23**, 1566). In the samples of it which I have prepared, I have repeatedly noticed that an extremely short exposure to light is sufficient to turn the very pale-yellow crystals of the nitropiperonal an intense and most brilliant yellow on the surface.

In order to convert nitropiperonal into the corresponding acrylic acid, 10 grams of the pure substance was mixed with 7 grams of fused sodium acetate and 12 grams of acetic anhydride, and the whole heated to gentle boiling by means of an oil-bath for three hours. The dark-coloured product was boiled with potassium hydrate solution, filtered, acidified with hydrochloric acid, and the greyish precipitate which separated collected, well washed, and dried on a porous plate.

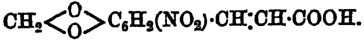
In order to further purify this crude product, it was converted into the methyl salt, by treatment with methyl alcohol and hydrogen chloride (see p. 156), and the salt thus obtained purified by recrystallisation from acetic acid and benzene. The methyl salt melted at 153°, and showed all the properties of the substance prepared from the acid, obtained by the nitration of piperonylacrylic acid.

However, to be certain of the identity, the salt was saponified by boiling with alcoholic potash, and the acid which separated on acidifying recrystallised from glacial acetic acid two or three times.

The resulting product possessed the same properties as the acid obtained from piperonylacrylic acid, and on heating in a capillary tube, showed the same behaviour.

The identity was further confirmed by the analysis :—

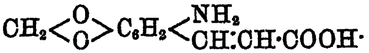
0·1688 gram substance gave 0·3138 gram CO_2 and 0·0489 gram H_2O.



$$\mathrm{CH_2}\!<\!\substack{\mathrm{O}\\ \mathrm{O}}\!>\!\mathrm{C_6H_3(NO_2)\cdot CH{:}CH\cdot COOH.}$$

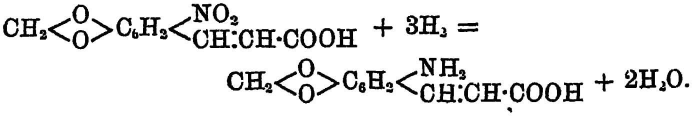
	Theory. $CH_2<^{O}_{O}>C_6H_3(NO_2)\cdot CH{:}CH\cdot COOH$.	Found.
C	50 63 per cent.	50·70 per cent.
H	2 95 ,,	3·17 ,,

Amidopiperonylacrylic Acid,



$$\mathrm{CH_2}\!<\!\substack{\mathrm{O}\\ \mathrm{O}}\!>\!\mathrm{C_6H_3}\!<\!\substack{\mathrm{NH_2}\\ \mathrm{CH{:}CH\cdot COOH}}\cdot$$

The nitro-group in nitropiperonylacrylic acid is readily reduced by ferrous hydrate with formation of amidopiperonylacrylic acid, thus:—



$$\mathrm{CH_2}\!<\!\substack{\mathrm{O}\\ \mathrm{O}}\!>\!\mathrm{C_6H_3}\!<\!\substack{\mathrm{NO_2}\\ \mathrm{CH{:}CH\cdot COOH}} + 3\mathrm{H_2} =$$
$$\mathrm{CH_2}\!<\!\substack{\mathrm{O}\\ \mathrm{O}}\!>\!\mathrm{C_6H_3}\!<\!\substack{\mathrm{NH_2}\\ \mathrm{CH{:}CH\cdot COOH}} + 2\mathrm{H_2O}.$$

The reduction was carried out as follows:—

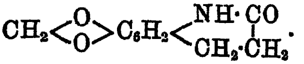
The pure nitro-acid (1 part) was dissolved in an excess of ammonia, the solution heated to boiling, a hot solution of ferrous sulphate (9 parts) mixed with excess of ammonia poured in, and the whole heated to boiling for about 10 minutes. The dark-coloured product was filtered, and the clear, brown solution evaporated to a small bulk, again filtered, and rendered slightly acid by the addition of hydrochloric acid. The red precipitate which was deposited was collected, washed with water, dried on a porous plate, and recrystallised from alcohol. The brownish, needle-shaped crystals then obtained gave the following numbers on analysis:—

0·1566 gram substance gave 0·3331 gram CO_2 and 0·0633 gram H_2O.

	Theory for $C_{10}H_9NO_6$.	Found.
C	58·06 per cent.	57·97 per cent.
H	4·63 ,,	4·34 ,,

Amidopiperonylacrylic acid melts at 205—207° with decomposition. It is readily soluble in acetic acid, less so in methyl and ethyl alcohol, sparingly in chloroform and light petroleum. It crystallises from its solution in alcohol in small, brownish needles; it is a very feeble acid.

Ethylamidopiperonyl-ω-carboxylic Anhydride,



$$\mathrm{CH_2}\!<\!\substack{\mathrm{O}\\ \mathrm{O}}\!>\!\mathrm{C_6H_2}\!<\!\substack{\mathrm{NH\cdot CO}\\ \mathrm{CH_2\cdot CH_2}}.$$

This substance is best prepared by reducing the ethyl or methyl salt of nitropiperonylacrylic acid with zinc or tin and hydrochloric acid. The pure salt was suspended in alcohol, and a stream of dry hydrogen chloride passed in without cooling until the liquid was completely saturated and the whole of the salt had passed into solution. Pieces of tin were then added, and the mixture allowed to stand until no further action took place. As soon as the reduction was complete, the product was diluted with water, boiled to expel the alcohol, and the tin precipitated with sulphuretted hydrogen. The filtrate and the washings from the sulphide of tin were evaporated to a small bulk, made slightly alkaline with potassium hydrate solution, and repeatedly extracted with ether. After distilling off the ether, the brownish residue was dissolved in boiling water, and the solution filtered and allowed to stand. The crystalline precipitate which separated was collected, recrystallised from dilute hydrochloric acid, and analysed with the following result:—

0·1536 gram substance gave 0·3553 gram CO_2 and 0·0700 gram H_2O.

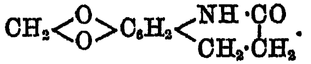
0·1541 gram substance gave 9·4 c.c. nitrogen; $t = 10°$; bar. = 764 mm.

	Theory for $C_{10}H_9NO_3$.	Found.
C.........	62·82 per cent.	63·08 per cent.
H.........	4·71 „	5·06 „
N	7·33 „	7·34 „

Ethylamidopiperonylcarboxylic anhydride melts at about 235° with slight previous softening. It is readily soluble in methyl alcohol, ethyl alcohol, and chloroform; very readily in acetic acid, but only sparingly in benzene and light petroleum. It dissolves very readily also in hot 50 per cent. hydrochloric acid, but does not appear to be converted into a nitroso-compound on the addition of sodium nitrite to this solution.

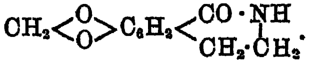
Ethylamidopiperonylcarboxylic anhydride is isomeric with the ω-amidoethylpiperonylcarboxylic anhydride obtained from berberine (Trans., **57**, 1013). The isomerism of the two compounds is readily understood with the help of the following formulæ:—

Ethylamidopiperonylcarboxylic anhydride................



$CH_2<\substack{O\\O}>C_6H_2<\substack{NH\cdot CO\\CH_2\cdot CH_2}$.

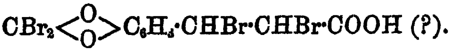
ω-Amidoethylpiperonylcarboxylic anhydride..........



$CH_2<\substack{O\\O}>C_6H_2<\substack{CO\cdot NH\\CH_2\cdot CH_2}$.

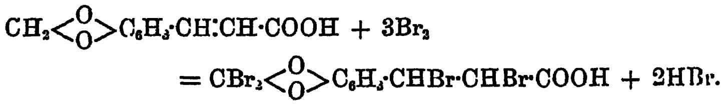
These two substances resemble each other in a marked degree, the former being, however, less soluble, and melting at a higher temperature than ω-amidoethylpiperonylcarboxylic anhydride (m. p. 181—182°).

Tetrabromopiperonylacrylic acid,



$$CBr_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_3\cdot CHBr\cdot CHBr\cdot COOH\ (?).$$

This tetrabromo-derivative was prepared by exposing finely-powdered piperonylacrylic acid under a bell glass to the fumes of excess of bromine for 24 hours. On lifting the bell glass, much hydrogen bromide escaped, showing that substitution had taken place, and a carefully conducted quantitative experiment proved that 4 atoms of bromine had been taken up, thus:—



$$CH_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_3\cdot CH{:}CH\cdot COOH + 3Br_2$$

$$= CBr_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_3\cdot CHBr\cdot CHBr\cdot COOH + 2HBr.$$

The dark-coloured product was placed over caustic potash in a vacuum desiccator until quite free from excess of bromine, and then rapidly dissolved in boiling benzene. During this operation, small quantities of hydrogen bromide were evolved, and the filtered solution, on standing, deposited a white, crystalline powder.

The analysis of a sample of the substance, dried over caustic potash in a vacuum, gave:—

0·3467 gram substance gave 0·2970 gram CO_2 and 0·0514 gram H_2O.

0·2436 gram substance gave 0·3586 gram AgBr.

	Theory for $C_{10}H_6Br_4O_4$.	Found.
C	23·53 per cent.	23·25 per cent.
H	1·17 „	1·64 „
Br	62·74 „	62·64 „

Tetrabromopiperonylacrylic acid melts at about 188° with decomposition. It is very soluble in alcohol and hot benzene, but only sparingly in the latter solvent in the cold.

Action of Potassium Hydrate on Tetrabromopiperonylacrylic Acid.

The tetrabromo-acid is readily decomposed by alcoholic or aqueous potassium hydrate with formation of a variety of substances which it was found very difficult to separate.

The best results were obtained in the following way:—

1. *Action of an Aqueous Solution of Potassium Hydrate.*—A considerable quantity of the tetrabrominated acid was dissolved in a mode-

rately strong aqueous solution of potassium hydrate (containing $1\frac{1}{2}$ times the calculated amount of KOH necessary to remove all the bromine). During this operation, a quantity of a white neutral substance separated; this was collected, washed with water, dried at 100°, and recrystallised, once from glacial acetic acid and twice from chloroform. The analysis gave the following numbers:—

0·1470 gram substance gave 0·1500 gram CO_2 and 0·0216 gram H_2O.

0·1773 gram substance, heated with nitric acid and nitrate of silver at 180°, gave 0·2616 gram AgBr.

	Theory. $CBr_2<\substack{O\\O}>C_6H_3\cdot C_2H_2Br$.	Found.
C..........	28·04 per cent.	27·82 per cent.
H..........	1·29 „	1·63 „
Br..........	62·34 „	62·78 „

This beautiful substance crystallises from chloroform in colourless, glistening prisms which melt at 185·5°. Its formation takes place according to the equation

$$CBr_2<\substack{O\\O}>C_6H_3\cdot CHBr\cdot CHBr\cdot COOK + 2KOH$$
$$= CBr_2<\substack{O\\O}>C_6H_3\cdot C_2H_2Br + KBr + K_2CO_3 + H_2O,$$

and its constitution may be represented by one of the two following formulæ:—

I.	II.
$CBr_2<\substack{O\\O}>C_6H_3\cdot CH{:}CHBr$,	$CBr_2<\substack{O\\O}>C_6H_3\cdot CBr{:}CH_2$,

of which formula II appears to be the more probable. This compound may therefore be called *tribromopiperonylethylene*.

The alkaline solution, which was separated from the crystals of the crude tribromo-compound, as already described, gives, on the addition of an acid, a copious precipitate of a mixture of brominated acids, which appear to be approximately of the same composition as those obtained by the action of alcoholic potash on the tetrabromo-acid, and the separation of which is described below.

2. *Action of Alcoholic Potash on the Tetrabromo-acid.*—15 grams of the tetrabromo-acid was dissolved in alcohol, and the solution gradually mixed with a solution of potassium hydrate in alcohol containing $1\frac{1}{2}$ times the quantity of KOH necessary for the removal of the whole of the bromine. The product was boiled in a reflux apparatus for about 10 minutes, a considerable quantity of water

added, and a small quantity of an oily, neutral substance, which smelt strongly of aniseed (and which will be referred to later on), extracted with ether. The alkaline solution was then acidified with dilute sulphuric acid, the white, curdy precipitate which separated collected, washed with water, and boiled with a large excess of aqueous potassium hydrate for half an hour; the solution was again precipitated, the precipitate collected, washed, redissolved in potash, and again heated to boiling, this operation being repeated three times.

The final product was purified by repeated fractional crystallisation from glacial acetic acid, and then separated into three substances, melting respectively at 188°, 210—211°, and 250° (approximately); the latter, being obtained only in very small quantity, was not further examined.

The substance melting at 188° gave, on analysis, the following numbers:—

I. 0·1350 gram substance gave 0·1602 gram CO_2 and 0·0185 gram H_2O.

0·1667 gram substance gave 0·2128 gram AgBr (by Carius' method).

II. 0·1570 gram substance gave 0·1730 gram CO_2 and 0·0210 gram H_2O.

	Theory. $C_{10}H_5Br_3O_4$.	Found. I.	Found. II.
C	27·97 per cent.	28·55	30·05 per cent.
H........	1·17 „	1·34	1·48 „
Br.......	55·94 „	53·12	— „

The substance melting at 210—211° is more sparingly soluble in glacial acetic acid than the above substance melting at 188°.

It gave on analysis the numbers:—

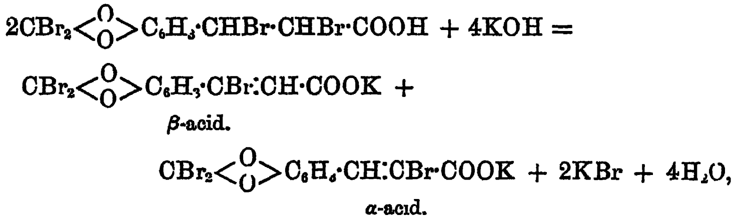
I. 0·1316 gram substance gave 0·1306 gram CO_2 and 0·0184 gram H_2O.

0·2009 gram substance gave 0·2603 gram AgBr (by Carius' method).

II. 0·1364 gram substance gave 0·1453 gram CO_2 and 0·0136 gram H_2O.

	Theory. $C_{10}H_5Br_3O_4$.	Found. I.	Found. II.
C	27·97 per cent.	27·06	29·06 per cent.
H........	1·17 „	1·55	1·11 „
Br.......	55·94 „	55·11	— „

Although these analytical numbers are not so sharp as could be wished, it is extremely probable that the two acids are formed from the tetrabromo-acid in the manner represesented by the following equation :—



$$2\mathrm{CBr_2}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}COOH} + 4\mathrm{KOH} =$$

$$\underset{\beta\text{-acid.}}{\mathrm{CBr_2}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CBr{:}CH{\cdot}COOK}} +$$

$$\underset{\alpha\text{-acid.}}{\mathrm{CBr_2}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{C_6H_3{\cdot}CH{:}CBr{\cdot}COOK}} + 2\mathrm{KBr} + 4\mathrm{H_2O},$$

the reaction being exactly similar to the formation of α- and β-monobromocinnamic acids by the action of caustic potash on phenyldibromopropionic acid, $C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}COOH$, and I therefore propose in the meantime to call the more soluble acid, melting at 188°, *β-tribromopiperonylacrylic acid*, and the acid melting at 210—211°, *α-tribromopiperonylacrylic acid*. Both of these acids behave similarly when treated with solvents; they are both sparingly soluble in boiling benzene and cold acetic acid, readily soluble in boiling acetic acid.

In the description of the separation of the products of the action of alcoholic potash on the tetrabromo-acid (see above), mention was made of an oily, neutral substance, which was removed by extraction with ether (p. 162). On distilling off the ether and allowing the residue to stand over sulphuric acid in a vacuum desiccator, a semisolid mass was obtained, which, on spreading on a porous plate, was readily separated from oily mother liquor.

The resulting light-yellow mass was repeatedly recrystallised from 90 per cent. methyl alcohol, and thus obtained in the form of microscopic, colourless needles, which on analysis gave the following numbers :—

0·1891 gram substance gave 0·2490 gram CO_2 and 0·0408 gram H_2O.

0·1570 gram substance gave 0·1902 gram AgBr (by Carius' method).

	Theory. $C_9H_6Br_2O_2$.	Found.
C	35·29	35·85
H	1·96	2·36
Br	52·28	51·84

This substance melts at 85°. It is readily soluble in acetic acid, methyl and ethyl alcohols, ether, and benzene, but almost insoluble in light petroleum. When heated in small quantities, it distils with decomposition, yielding an oily distillate which solidifies on cooling.

The formation of this compound (for which I propose the name dibromopiperonylethylene) from the tetrabrominated acid is remarkable, and must be due to the reducing action of the alcoholic potash employed, thus:—

$$CBr_2{<}\substack{O\\O}{>}C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}COOH + 4KOH + H_2 =$$

$$CBr_2{<}\substack{O\\O}{>}C_6H_3{\cdot}CH{:}CH_2 + 2KBr + K_2CO_3 + 3H_2O.$$

Dibromopiperonylethylene.

The amount of this substance produced in the above reaction is very small.

Piperonyloin, $CH_2{<}\substack{O\\O}{>}C_6H_3{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_3{<}\substack{O\\O}{>}CH_2$.

When digested in alcoholic solution with potassium cyanide, piperonal is readily converted into the isomeric piperonyloin, just as benzaldehyde, under similar conditions, yields benzoin. 5 grams of piperonal are dissolved in 20 grams of 50 per cent. alcohol, 2 grams of pure potassium cyanide added, and the whole heated to gentle boiling in a flask connected with a reflux apparatus for 3½ hours. After standing for 12 hours, the yellow, crystalline mass which separates is collected and recrystallised, first from ethyl alcohol, then from methyl alcohol, and dried at 100°.

The analysis gave the following numbers:—

0·1390 gram substance gave 0·3246 gram CO_2 and 0·0530 gram H_2O.

	Theory $C_{16}H_{12}O_6$.	Found
C	64·00 per cent.	63·64 per cent.
H	4·00 ,,	4·32 ,,
O	32·00 ,,	32·04 ,,

Piperonyloin melts at 120°. It is readily soluble in chloroform, methyl and ethyl alcohols, and acetic acid, sparingly soluble in ether; the hot solution in alcohol deposits the substance on cooling in deep-yellow, nodular masses.

Piperonyloin is very readily oxidised by nitric acid, with formation of much oxalic acid, and all attempts to prepare the corresponding piperonil, $CH_2{<}\substack{O\\O}{>}C_6H_3{\cdot}CO{\cdot}CO{\cdot}C_6H_3{<}\substack{O\\O}{>}CH_2$, have so far given nothing but negative results.

The yield of piperonyloin produced in the above reaction is very good, but if larger quantities are employed in one operation, very unsatisfactory results are obtained.

XVIII.—*The α- and β-Modifications of Benzene Hexachloride.*

By F. E. Matthews, Ph.D.

Some results obtained by Professor McLeod, by the simultaneous action of chlorine and sodium hydrate on some inorganic substances, led me to investigate the action of these agents on some organic compounds.

The substance chosen for commencing the investigation was benzene, and although the reaction did not proceed in the direction which was expected, yet the results obtained seem of sufficient importance to warrant publication, the more so as the reaction appears to be of general application with respect to a large number of aromatic hydrocarbons and their derivatives.

Some benzene was placed upon the surface of a dilute solution (about 1 per cent.) of sodium hydrate in a flask, and, without any special precautions being taken, a stream of chlorine was passed into the mixture. After the first few bubbles of gas had been passed, the benzene lost its transparency and very soon became bright yellow; on continuing to pass in chlorine for some time, the benzene evidently increased considerably in density, and at length fell to the bottom of the sodium hydrate solution in the form of a heavy, yellow oil. More benzene was then added, and the stream of chlorine continued till the second portion of benzene also sank to the bottom of the flask. It was then corked up and placed outside the laboratory for the night, to see whether any solid would crystallise out on exposure to the low temperature. Next morning about one-half of the oil had been converted into large masses of white crystals, and the oil still remaining had become colourless. The crystals were separated from the oil and the aqueous solution, and, after being well washed with water, were dried upon a porous plate; the oil was again treated with dilute sodium hydrate solution and chlorine, and was finally almost entirely converted into the crystalline solid.

A chlorine determination was made upon the air-dried crystals with the following result:—

0·2035 gram of the substance burnt with ignited Iceland spar gave 0·5773 gram AgCl.

Found.	Theory for $C_6H_6Cl_6$.
70·17	73·19 per cent. chlorine.

This high percentage of chlorine showed almost conclusively that the substance was approximately pure benzene hexachloride, the more so as the melting point of the crude substance was found to be 148—151° (uncorr.), and the melting point of the α-$C_6H_6Cl_6$ is given as 157° (corr.).

As these results pointed simply to the formation of an additive compound of benzene, and as there was no apparent reason for the use of the sodium hydrate, the action of chlorine on a mixture of benzene and water was tried. The reaction was found to proceed on the same lines as before, but although considerable quantities of the hexachloride have been made by this method, the results never seemed quite so satisfactory as when sodium hydrate solution was employed, the amount of uncrystallisable oil being greater; the process with water alone has been abandoned, therefore, in favour of that first described.

The following method has been found to be the most convenient for the preparation of crude benzene hexachloride, as it does not depend at all on the temperature of the mixture, and equally good results are obtained either in bright sunlight or in darkness, and further, the rate of formation of the substance practically depends only on the rate at which the chlorine can be generated.

A series of three or four flasks, a convenient size being about 12 ounces, is arranged with the delivery tube from one flask passing to the bottom of the next. The flasks are about half filled with a 1 per cent. solution of caustic soda, and 20 to 40 grams of benzene are added to each flask; the flasks are connected, and a rapid stream of chlorine is passed through the apparatus, when it will be found that absorption is practically complete in the first flask for a considerable time. The temperature rises considerably in the first flask, and at length crystals begin to appear, and the mixture becomes saturated with chlorine. When the flask in which the chlorine is generated becomes exhausted, the flask or flasks which have been saturated should be detached, and allowed to stand for 12 hours in a cool place. The crystals may then be removed from the oily and aqueous portions, most conveniently by means of a coarse muslin filter; fresh benzene, and some more sodium hydrate may then be added to the oily layer, and the saturation continued as before. By this method of working, the amount of substitution products produced seems to be very small, although after the chlorine has been passed through the same portion of benzene several times, it is noticed that the oil does not crystallise so readily, doubtless on account of the formation of substitution compounds.

The crude substance obtained by this process is a colourless, crystalline mass, closely resembling in its properties the benzene hexachloride prepared by other methods. It is soluble in all the ordinary organic solvents, but crystallises best from about 80 per cent. acetic acid. After several recrystallisations, the melting point is 157° (corr.), and no further alteration takes place even on repeated recrystallisation.

The behaviour, both of the crude substance and of the recrystallised portions, when the melting point is determined, shows that the substance is a mixture; although the melting point, 157°, is perfectly definite, yet the substance, even after repeated recrystallisation from various solvents, always leaves a residue which does not melt, or dissolve in the fused portion, till a much higher temperature is reached. It seemed probable that the difficultly fusible portion was the β-benzene hexachloride described by Meunier (*Bull. Soc. Chim.*, **41**, 530; and *Compt. rend.*, **98**, 436), and by Schüpphaus (*Ber.* **17**, 2256).

Many attempts were made to obtain one of the substances free from the other by fractional crystallisation, but although, as will be seen later, they differ greatly in their solubility in the ordinary solvents, it was not found possible to obtain either of them in a state of purity.

The method of preparing the β-compound described by Meunier was next tried, namely, by boiling the mixture of α- and β-substances with alcoholic potassium cyanide for 30 hours. By this means, the α-substance is entirely decomposed, whilst the more stable β-compound is able to resist the action. It was thus found possible, but only with great difficulty, to obtain the β-substance in a state of purity; the chief difficulty consisting in extracting the undecomposed β-derivative from the large amount of tarry matter produced by the decomposition of the α-compound.* Alcohol was found to be the most suitable solvent, as although the β-compound was not very readily soluble in it on boiling, yet the tarry products dissolved in it much less readily than in any other solvent tried. The crystals deposited by the alcoholic solution were purified by careful sublimation, as described by Meunier. By Meunier's process of separation, it will be seen that the whole of the α-substance, constituting about 70 per cent. of the crude benzene hexachloride, is lost; moreover, the yield of the β-compound is far from satisfactory.

A much better method of separating the two substances was found to consist in distilling the crude $C_6H_6Cl_6$ in a current of steam, in which the α-compound alone is volatile; this process, although somewhat slow, is a quantitative one, as in this way the α-compound can be entirely separated, for the most part collecting in the Liebig's condenser, leaving the β-compound behind. The latter can then be obtained in a state of purity by a single crystallisation from alcohol, without any subsequent sublimation being necessary.

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* The only substances I definitely recognised amongst the decomposition products of the α-derivative by Meunier's process were diphenyl and ammonium cyanide. From the odour, I suspected the presence of naphthalene, but have not been able to identify it.

The steam-distilled α-derivative was further purified by recrystallisation either from moderately strong alcohol or from about 80 per cent. acetic acid; it forms very characteristic crystals shaped like fern-leaves, and melts quite constantly at 157° (corr.) without leaving any unmelted residue.

Two determinations of the molecular weight of the α-substance were made by Raoult's method, the first in benzene solution and the second in acetic acid, as it was thought possible that some decomposition might take place in benzene solution. The results were as follows:—

	I. In benzene.	II. In acetic acid.	Theory for $C_6H_6Cl_6$.
Wt. of substance..	1·3142 grams.	3·2744 grams.	
Wt. of solvent....	100 ,,	100 ,,	
Depression of freezing point of solvent	0·26	0·595	
Molecular weight..	248	270	291

There does not seem to be any record of α-benzene hexachloride having been previously obtained free from the β-derivative. It is a colourless substance, insoluble in water, but readily soluble in all the ordinary organic solvents. It is very stable, and resists the action of most reagents, except that of alcoholic potash or soda, or of alcoholic potassium cyanide at the boiling temperature. Fuming nitric acid is without action, the substance merely dissolving when heated, and crystallising out again on cooling. It is not altered by long-continued boiling with chromic acid; with potassium permanganate, only a very slight action takes place even on heating. The substance resisted all attempts to further chlorinate it. Aqueous ammonia is without action on it, as is a boiling alcoholic solution of silver nitrate. On distilling it over zinc-dust, a colourless, crystalline compound was obtained smelling strongly of diphenyl. On heating the substance above its melting point, it evolves hydrogen chloride, and forms a liquid product, probably $C_6H_3Cl_3$ [1 : 2 : 4].

The β-benzene hexachloride left as a residue, after the α-modification has been distilled off, when recrystallised from alcohol, exactly resembles the substance prepared by Meunier's method. It forms small and very brilliant crystals which are almost colourless, and on careful sublimation, without previous fusion, it forms a snow-white powder consisting of microscopic crystals.

It is even more stable than the α-compound, not only being unacted on by all the reagents incapable of decomposing the α-modification, but even boiling alcoholic potassium cyanide does not affect it, and it is only completely decomposed by boiling for three hours with alcoholic potash.

It is very much less soluble than the α-modification in all solvents tried, although strangely the two substances do not appear to be separable by fractional crystallisation. Its solubility in acetic acid and in benzene was determined.

100 grams of acetic acid at 15·6° dissolve 0·289 gram (mean of two experiments).

100 grams of benzene at 22° dissolve 1·204 grams (mean of two experiments).

A molecular weight determination was made in benzene solution by Raoult's method (acetic acid cannot be used owing to the insolubility of the substance).

0·0752 gram of substance dissolved in 15·1182 grams of benzene caused a depression of 0·085° in the freezing point.

Found.	Theory.
287	291

The substance dissolves readily in hot benzene and acetic acid, but is much less soluble in boiling alcohol.

An attempt was made to determine its vapour density by Victor Meyer's method, but from the dissociation of the substance no definite results as to its molecular weight were obtained, but the figures are interesting as a study of dissociation.

	I.	II.	III.
Temperature of bath*.	295°.	330°.	370°.
Wt. of substance..	0·0963 gram	0·0686 gram	0·0491 gram.
Volume of gas collected	22·75 c.c.	17·84 c.c.	17·04 c.c.
Height of barometer	739·4 mm.	739·4 mm.	739·4 mm.
Temperature of gas	13°	12·5°	13°
Vapour density ...	3·43	3·24	2·44

$$\text{Theory for } \frac{C_6H_6Cl_6}{4} = C_6H_3Cl_3 + 3HCl = 2{\cdot}52.$$

Meunier (by Hofmann's method) obtained the vapour densities 9·365 and 9·207 (theory for $C_6H_6Cl_6$, 10·08). Thus, at about 180°, dissociation has already begun, and steadily increases with the rise of temperature, till at 370°, the dissociation into 4 mols. is complete.

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* The temperatures were taken by means of one of Muller's mercury thermometers containing nitrogen gas under pressure.

From the above results, and from the fact that the β-modification is capable of being sublimed, it was attempted to synthesise the substance from $C_6H_3Cl_3$ [1 : 2 : 4] and hydrogen chloride, but, although several methods have been tried, at present without success.

Both modifications of benzene hexachloride yield the same trichlorobenzene [1 : 2 : 4], when treated with hot alcoholic potash, although the β-modification possesses much greater stability. The two substances were decomposed side by side in two flasks; in the case of the α-compound the reaction was complete after a few minutes' boiling; the β-compound was digested for three hours. The products of the reactions were diluted, acidified, and extracted with ether; on distilling off the ether, two oils of similar odour were left. They were placed in a desiccator and allowed to stand for some days, but neither oil showed signs of crystallisation. To further prove the identity of the two, they were both converted into nitro-derivatives by boiling with fuming nitric acid. The nitro-derivatives were precipitated with water, washed, and recrystallised from aqueous alcohol. Both solutions deposited crystals of almost colourless, interlaced needles, which were evidently the same substance. The melting points were taken: that of the $C_6H_2Cl_3(NO_2)$, obtained from α-benzene hexachloride melted at 57·5—58°; the nitro-derivative obtained from the β-hexachloride melted at 58—58·5°; the melting point of $C_6H_2Cl_3(NO_2)$ is given by Beilstein as 58°. Both hexachlorides therefore yield the same trichlorobenzene on treatment with alcoholic potash.

There seems to be very little doubt that both the α- and β-hexachlorides of benzene have the composition $C_6H_6Cl_6$. All the evidence we at present possess goes to show that the two compounds are isomeric, namely, first, the analyses of Meunier and Schupphaus; second, the vapour density determinations made by Meunier; third, the molecular weight determinations by Raoult's method*; fourth, the fact that both compounds yield the same trichlorobenzene when acted on by alcoholic potash.

The reason for the existence of two isomeric hexachlorides of benzene is not very clearly shown by any of the benzene formulæ at present proposed, unless we assume that an intramolecular change has taken place, and that some of the carbon atoms in the molecule of one of the addition products are connected with 2 atoms of chlorine and others with 2 atoms of hydrogen.

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* I have recently found that the molecular weights of α- and β-benzene hexachlorides have also been determined by Paternò and Nasini (*Gazzetta*, 19, 195—209), and that their figures give $C_6H_6Cl_6$ as the formula for both compounds.

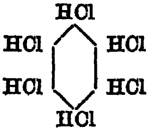
That some intramolecular change had taken place in the formation of one of the hexachlorides did not appear improbable when the substances were made by either of the older methods, either by passing chlorine into boiling benzene or into benzene exposed to direct sunlight, but the chance of any such change was lessened by the formation of the same trichlorobenzene when the substances were acted on by alcoholic potash; now that the hexachlorides can be prepared, if necessary, in a freezing mixture and in darkness, the chance of any such change is greatly decreased.

From some work that I am at present engaged upon, but which is not yet quite ready for publication, it seems that monochlorobenzene yields hexachlor-addition products similar to those of benzene, $[C_6H_5Cl_7]$, which on treatment with alcoholic potash yield tetrachlorobenzene [1 : 3 : 4 : 5]. This shows that in the hexachlorides of chlorobenzene at least four of the carbon atoms are directly connected to chlorine, and thus greatly increases the probability that in both the α- and β-benzene hexachlorides each carbon atom is directly connected with an atom of chlorine.

I have made many attempts to convert these substances from one modification to the other, but hitherto without success.

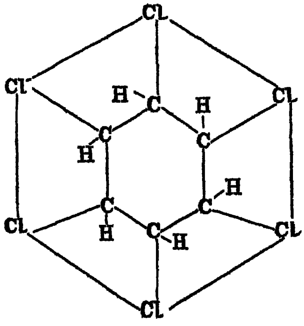
It seems rather early to hazard a speculation as to the constitution of these two substances, but as all the benzene formulæ fail to explain why two symmetrical isomers of the composition $C_6H_6Cl_6$ should exist, I think a certain amount of speculation is justifiable.

It seems to me not impossible that the α-compound may have the constitution—



,

and that the β-compound may be represented by the formula



that is to say, that the chlorine has become triadic, and has formed a second ring consisting of 6 chlorine atoms. This hypothesis would go far towards explaining the superior stability of the β-substance.

I have found that bromine acts additively under similar conditions to chlorine, and further, that addition compounds of other derivatives of benzene, toluene, xylene, naphthalene, &c., and their derivatives may be obtained by slight modifications in the method of working.

These reactions are being investigated, and I hope to contribute the results in a future paper to the Chemical Society.

Royal Indian Engineering College,
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XIX.—*The Action of Heat on Ethylic β-Amidocrotonate.* Part I.

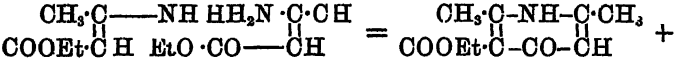
By J. NORMAN COLLIE, F.R.S.E.

SOME years ago (*Annalen*, **226**, 297), whilst working with ethylic β-amidocrotonate, I noticed that, during its purification by distillation under reduced pressure, a crystalline compound of the formula $C_{10}H_{13}NO_3$ was always produced in small quantities, and remained behind in the fractionating flask, the reaction taking place according to the following equation:—

$$2C_6H_{11}NO_2 = C_{10}H_{13}NO_3 + NH_3 + C_2H_5{\cdot}OH.$$

This condensation product was found to be the ethylic salt of an acid, $C_8H_9NO_3$, which, from its properties, was considered to be the monocarboxylic acid of a hydroxylutidine. Owing to the small quantities obtained, the investigation was carried no further. Since then, having had to work with large amounts of ethylic β-amidocrotonate, a further supply of the condensation product has been obtained, and a more exact study of its derivatives has been possible. I now find that this acid, on heating, yields carbon dioxide and a substance C_7H_9NO, which is identical in all respects with the αα′-dimethylpyridone obtained by Haitinger from dehydracetic acid (*Ber.*, **18**, 452), and also by Conrad and Guthzeit (*Ber.*, **20**, 159), by heating lutidonedicarboxylic acid.

The condensation by heat of the ethylic β-amidocrotonate is therefore as follows:—



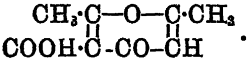
$$\begin{array}{l}\mathrm{CH_3\cdot C{-\!\!-\!\!-}NH\ HH_2N\cdot C\cdot CH}\\ \mathrm{COOEt\cdot CH\ \ EtO\cdot CO{-\!\!-\!\!-}CH}\end{array} = \begin{array}{l}\mathrm{CH_3\cdot C{-}NH{-}C\cdot CH_3}\\ \mathrm{COOEt\cdot C{-}CO{-}CH}\end{array} + \mathrm{NH_3 + C_2H_5\cdot OH.}$$

Ethylic β-amidocrotonate. Ethylic dimethylpyridonemonocarboxylate.

This partial decomposition by heat seemed, at first sight, to be similar to that which ethylic acetoacetate undergoes in its conversion into dehydracetic acid during distillation:—

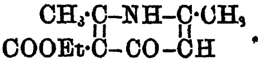
$$2C_6H_{10}O_3 = C_8H_8O_4 + 2C_2H_5\cdot OH,$$

especially if the formula which Perkin suggests for dehydracetic acid be the true one:—



$$\begin{array}{l}\mathrm{CH_3\cdot C{-}O{-}C\cdot CH_3}\\ \mathrm{COOH\cdot C{-}CO{-}CH}\end{array}.$$

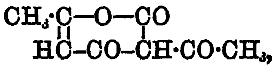
Dehydracetic acid (?).



$$\begin{array}{l}\mathrm{CH_3\cdot C{-}NH{-}C\cdot CH_3}\\ \mathrm{COOEt\cdot C{-}CO{-}CH}\end{array}.$$

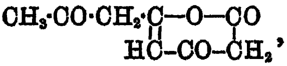
Dimethylpyridonemonocarboxylic ethyl ether.

But, according to Ostwald, dehydracetic acid does not contain a COOH group, as its conductivity is far less than that required by a true organic acid; therefore Feist, in his interesting paper on dehydracetic acid (*Annalen*, **257**, 253), suggests the following formula:—



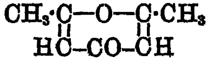
$$\begin{array}{l}\mathrm{CH_3\cdot C{-}O{-}CO}\\ \mathrm{\ \ \ \ \ HC{-}CO{-}CH\cdot CO\cdot CH_3,}\end{array}$$

and in a note on the constitution of dehydracetic acid, appended to this paper, I suggest an alternative one:—



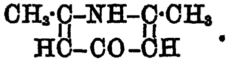
$$\begin{array}{l}\mathrm{CH_3\cdot CO\cdot CH_2\cdot C{-}O{-}CO}\\ \mathrm{\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ HC{-}CO{-}CH_2,}\end{array}$$

and if either of these last two formulæ be correct for dehydracetic acid, then the action of heat on the ethylic β-amidocrotonate will not be analogous to the action of heat on ethylic acetoacetate, although, by a series of simple reactions, the one is converted into αα′-dimethylpyrone, and the other into αα′-dimethylpyridone.



$$\begin{array}{l}\mathrm{CH_3\cdot C{-}O{-}C\cdot CH_3}\\ \mathrm{\ \ \ \ \ HC{-}CO{-}CH}\end{array}.$$

αα-Dimethylpyrone.



$$\begin{array}{l}\mathrm{CH_3\cdot C{-}NH{-}C\cdot CH_3}\\ \mathrm{\ \ \ \ \ HC{-}CO{-}CH}\end{array}.$$

αα′-Dimethylpyridone.

This αα′-dimethylpyridone, when treated with pentachloride of phosphorus, yields a chlorolutidine, which, on reduction with nascent hydrogen, yields αα′-dimethylpyridine in very small quantity.

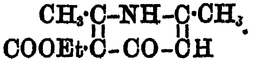
Although the reduction of this chlorolutidine is only effected in very small amount, after many days treatment with tin and hydrochloric acid, still the production of a lutidine by this means is of interest, as it affords a method by which a true pyridine derivative, that is, *αα'*-dimethylpyridine, may be produced from ethyl acetoacetate by a set of simple reactions, all of which take place at no very high temperature. The lutidine thus produced has been identified with lutidines obtained by the following methods:—

(1.) By the distillation of the potassium salt of lutidonecarboxylic acid with excess of caustic potash.
(2.) By heating the chlorolutidine (mentioned above) with zinc-dust in an atmosphere of hydrogen.
(3.) By heating the chlorolutidine obtained from dehydracetic acid by Haitinger's method with zinc-dust.
(4.) A lutidine obtained by W. Ramsay from bone oil, b. p. 143—144.°

By oxidation of the lutidine from ethylic *β*-amidocrotonate with potassium permanganate, a pyridinedicarboxylic acid was obtained melting at 235° (corr.), which, on heating, gave pyridine, showing that it was dipicolinic acid or the *αα'*-pyridinecarboxylic acid.

EXPERIMENTAL PART.

Ethylic Lutidonemonocarboxylate,



$$\begin{array}{c}CH_3\cdot C\!-\!NH\!-\!C\cdot CH_3 \\ \| \qquad\qquad \| \\ COOEt\cdot C\!-\!CO\!-\!CH\end{array}.$$

The preparation and most of the properties of this substance have been already noticed in my former paper (*loc. cit.*).

The melting point is 163—164° (corr.),* and the boiling point lies between 240° and 250° with slight decomposition; I may here mention that it is *soluble* in water, as in my former paper, through an error, it was stated to be *insoluble*.

It does not react with acetic anhydride, even after many hours heating at 140—150°; neither does it form a compound with phenyl hydrazine or with hydroxylamine, and therefore differs from dehydracetic acid in this respect.

A determination of the molecular weight by the Raoult method showed a very marked rise when more than a small quantity of the ethereal salt was used, the results being as follows:—

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* All the melting and boiling points mentioned in this paper were taken with a set of Anschutz thermometers supplied by Desaga, of Heidelberg.

Substance taken.	Acetic acid taken.	Depression.	$\frac{39}{\text{Mol. depression.}}$	$C_{10}H_{13}NO_3$, mol. weight.
0·1000	27·65	0·074	190	195
0·2935	27·65	0·200	207	195
0·5485	27·65	0·370	209	195
0·8145	30·67	0·440	235	195
1·2775	35·13	0·400	354	195

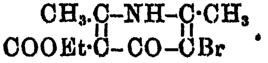
Treated with bromine in acetic acid, a reaction occurs at once, and the temperature rises slightly. 10 grams of the ethyl compound were dissolved in acetic acid, and 8 grams of bromine were carefully added. The mixture was poured into water, and sodium carbonate added till the solution was nearly neutral. A white crystalline bromine compound was precipitated which was separated by filtration, washed with water, and, after recrystallisation from alcohol and water, melted constantly at 249—250° (corr.). An analysis gave the following numbers:—

0·2850 gram substance gave 0·1955 gram AgBr = 29·20 per cent. bromine.

0·3010 gram substance gave 0·480 gram CO_2 and 0·122 gram H_2O. C = 43·49; H = 4·50.

	Calculated for $C_{11}H_{12}NO_3Br$.	Found. I.	Found. II.
C	43·79	—	43·49
H	4·38	—	4·50
Br..........	29·19	29·20	—

The substance is therefore a monosubstituted derivative, and probably has the following formula:—



$$\begin{array}{l} \mathrm{CH_3.C{-}NH{-}C{\cdot}CH_3} \\ \qquad\ \ \| \qquad\quad \| \\ \mathrm{COOEt{\cdot}C{-}CO{-}CBr} \end{array}.$$

During the purification, it was noticed that this bromine derivative is capable of crystallising in two distinct forms. If a strong solution is cooled in a test-tube, it sets to a mass of long, interwoven, needle-shaped crystals, and the test-tube may be inverted without the contents being spilt; but, after standing, the needle-shaped crystals gradually disappear, and a small layer of hard, granular crystals remain at the bottom of the tube.

The action of pentachloride of phosphorus on the ethylic lutidonemonocarboxylate was also tried. 20 grams of the compound were heated to 160°, and 22·5 grams of pentachloride of phosphorus was cautiously added. The mixture, on cooling, remained liquid, and, after the oxychloride of phosphorus had been removed by distillation, the residue was poured into water. The solution was neutralised with carbonate of soda, and extracted with ether. From the ethereal extract a pleasant smelling oil, b. p. 263--264° (corr.), was obtained.

0·3805 gram substance gave 0·2615 gram AgCl = 17·00 per cent. chlorine.

0·4110 gram substance gave 0·8430 gram CO_2 and 0·2070 gram H_2O. C = 55·96; H = 5·60.

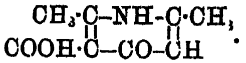
	Calculated for $C_{10}H_{12}NO_2Cl$.	Found. I.	Found. II.
C	56·21	—	55·96
H	5·62	—	5·60
Cl	16·62	17·00	—

The reaction therefore takes place as follows:—

$$C_{10}H_{13}NO_3 + PCl_5 = C_{10}H_{12}NO_2Cl + POCl_3 + HCl.$$

This chloride, when dissolved in alcohol and warmed with dilute soda solution, does not lose its chlorine, but is converted into the sodium salt of a chlorinated acid. This acid, when heated, readily parts with carbon dioxide leaving a chlorolutidine, b. p. 177—180°, which is identical with the chlorolutidine which is produced by the action of pentachloride of phosphorus on lutidone obtained by heating lutidonemonocarboxylic acid.

Lutidonemonocarboxylic Acid,



$$\begin{array}{l} CH_3\cdot C\text{–}NH\text{–}C\cdot CH \\ \qquad\ \ \| \qquad\qquad\ \| \\ COOH\cdot C\text{–}CO\text{–}CH \end{array}.$$

This compound has already been described in my former paper. It can be prepared by warming a solution of the ethereal salt with caustic soda solution and then precipitating the free acid with sulphuric acid. It is a crystalline compound, easily yielding salts. These salts do not seem, however, to be very stable, the barium salt being decomposed by carbon dioxide into barium carbonate and the free acid. The acid itself may be heated to 200° with strong sulphuric acid, and is reprecipitated unchanged on the addition of water.

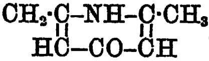
An attempt was made to convert this acid into dehydracetic acid by prolonged boiling with dilute sulphuric acid,

$$C_8H_9NO_3 + H_2O = C_8H_8O_4 + NH_3,$$

but without success, the acid remaining unchanged. When the acid is heated, it melts at 257—258° (corr.), and is quantitatively converted into carbon dioxide and $\alpha\alpha'$-dimethylpyridone,

$$C_8H_9NO_3 = C_7H_9NO + CO_2.$$

αα′-Dimethylpyridone,



$$\begin{array}{l} CH_2\cdot C\!-\!NH\!-\!C\cdot CH_3 \\ \quad\;\; \| \qquad\quad\;\; \| \\ \quad HC\!-\!CO\!-\!CH \end{array}.$$

This compound has been obtained by Conrad and Guthzeit by heating lutidonedicarboxylic acid (*Ber.*, **20**, 156). Haitinger also obtained it by heating dehydracetic acid with aqueous ammonia (*Ber.*, **18**, 452). They give the melting point as 225°. The compound produced by heating lutidonemonocarboxylic acid agreed in all respects with lutidone obtained by the above mentioned chemists (m. p. 225° or 231—232° corr.). A combustion gave C = 67·94; H = 7·42. Theory for C_7H_9NO, C = 68·29; H = 7·32.

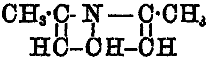
The platinochloride was also prepared. The melting point given by Haitinger is 224°; the melting point was found to be 230—231° (corr.), and an analysis gave Pt = 29 90.

Theory for $(C_7H_9NO,HCl)_2PtCl_4$, Pt = 29·67.

Some αα′-dimethylpyridone was also prepared from dehydracetic acid; on comparison, it was found to be identical in all respects with the compound mentioned above.

Pentachloride of phosphorus reacts at once with this lutidone, giving a chlorolutidine, b. p. 178—179°. Conrad and Epstein prepared this compound from the lutidone obtained by heating lutidonedicarboxylic acid (*Ber.*, **20**, 164). They also found the boiling point to be 178°. This chlorolutidine was therefore not analysed.

αα′-Dimethylpyridine or Lutidine,



$$\begin{array}{l} CH_3\cdot C\!-\!N\!-\!\!-\!C\cdot CH_3 \\ \quad\;\; \| \quad\; | \qquad \| \\ \quad HC\!-\!CH\!-\!CH \end{array}.$$

I have obtained this lutidine by four different methods.

(1.) By the action of nascent hydrogen on the chlorolutidine boiling at 178°. The chlorolutidine is hardly attacked by nascent hydrogen; still by the prolonged treatment with tin and fuming hydrochloric acid, a small amount of the lutidine is formed. By far the larger quantity of the chlorolutidine remains unchanged, and can be recovered from the solution on evaporation in the form of a beautifully crystalline double compound with stannous chloride, m. p. 108—109°.

0·350 gram substance took 29·00 c.c. decinormal $AgNO_3$ = 29·41 per cent. Cl.

Theory for 3Cl in $C_7H_8NCl,HCl,SnCl_2$ = 29·01 per cent. Cl.

The mother liquors, after the separation of most of the chlorolutidine in the form of the double compound with stannous chloride, were treated with a slight excess of caustic soda and a current of steam was then blown through. A small quantity of lutidine mixed with chlorolutidine distilled over. The amount was too small for the boiling point to be taken with accuracy, but it lay between 143° and 147°. This lutidine was converted, therefore, into the platinochloride. The salt melted at 209—211°.

0·200 gram substance gave 0·0625 gram Pt = 31·25 per cent. Pt.
0·321 gram substance gave 0·1005 gram Pt = 31·31 per cent. Pt.
Theory for $(C_7H_9N,HCl)_2PtCl_4$ = 31·20 per cent. Pt.

(2.) A better method for obtaining the lutidine is to pass the vapour of the chlorolutidine over heated zinc-dust in an atmosphere of hydrogen. In this way, a lutidine was obtained boiling between 144° and 145° (corr.),* and giving a platinochloride, melting at 210—212° (corr.). A combustion gave the following numbers:—

0·320 substance gave 0·9200 gram CO_2 and 0·2460 gram H_2O.

	Theory for C_7H_9N.	Found.
C	78·50	78·44
H	8·41	8·57

(3.) A lutidine identical with the above was obtained from the chlorolutidine made from dehydracetic acid, its boiling point, 144—145°, and the melting point of the platinochloride, 210—212°, being considered sufficient to rely upon. Haitinger, however, obtained a lutidine boiling at 148—151° by heating the *αα'*-dimethylpyridone (made from dehydracetic acid) with zinc-dust.

(4.) The potassium salt of the lutidonemonocarboxylic acid, when heated with excess of solid caustic potash, gives the same lutidine in small quantity.

The platinochloride melted at 208—210° and left, on ignition, 31·30 per cent. Pt.

I have also been able to compare this lutidine with one obtained by Professor Ramsay from bone oil, b. p. 143—144°. Both the crystalline form, as well as the melting point of the platinochloride 210—212°, were the same. The two lutidines are therefore doubtless identical.

Oxidation of αα'-Dimethylpyridine.

2 grams of this lutidine (obtained from the chlorolutidine) were oxidised with permanganate of potassium. After nearly the whole of the lutidine had been oxidised, the mixture was filtered to separate the precipitated manganese dioxide, and the filtrate evaporated, and

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* Epstein gives the boiling point of *αα'*-lutidine made by heating lutidonedicarboxylic acid with zinc-dust as 144—145°.

precipitated by silver nitrate. The silver salt was decomposed by sulphuretted hydrogen, and the resulting solution, on evaporation, yielded a crystalline acid. After recrystallisation from dry alcohol and ether, the acid was found to melt at 235—236° (corr.), and gave with ferric chloride a reddish-yellow coloration. When heated alone, a strong smell of pyridine was produced. The acid, on analysis, gave:—

0 222 gram substance gave 0·407 gram CO_2 and 0·061 gram H_2O.

	Calculated for $C_5H_3N(COOH)_2$.	Found.
C	50·29	50·00
H	2·99	3·05

The acid is therefore dipicolinic acid, and is the same as that obtained by Hantzsch (*Ber.*, **18**, 1744), and Epstein (*Ber.*, **19**, R. 18).

University College,
London.

XX.—*On the Constitution of Dehydracetic Acid.*

By J. Norman Collie, Ph.D., University College, London.

During an investigation of the action of heat on ethylic β-amidocrotonate (on which I have been engaged for some years) I was much struck with the partial decomposition this ethereal salt undergoes when distilled, yielding ethylic lutidonecarboxylate, a pyridine derivative.

This decomposition forcibly recalls the formation of dehydracetic acid from ethylic acetoacetate when the latter is heated, and the fact that dehydracetic acid itself gives lutidone when treated with ammonia still further increases the resemblance. I was naturally led, therefore, to inquire into the formulæ which various investigators have proposed for dehydracetic acid. This peculiar compound has for long been the subject of investigation, but the various formulæ which have been suggested are all open to criticism, as Feist, in his excellent paper on this acid (*Annalen*, **257**, 253), has shown; and as he discusses this question in detail, it is needless to again go over the ground. I shall, therefore, only take the formula given by Feist, and show where I think it is inadequate to explain all the known properties and reactions of dehydracetic acid.

Dehydracetic acid is formed by the action of heat on ethylic acetoacetate, alcohol, water, and ethylene being produced at the same time, the best process for its manufacture being to allow a slow stream of ethylic acetoacetate to run into an iron tube filled with pumice stone and heated in a combustion furnace. In this way, nearly the whole of the ether is converted into dehydracetic acid.

That dehydracetic acid is a true acid, containing the carboxyl group, was for some time thought to be the case. Ostwald, however, contradicts this,* showing that, from measurement of the conductivity of the acid, the dissociation constant obtained is about 200 times too small, as compared with the constant of such acids as salicylic acid. It therefore probably resembles the phenols or else compounds such as ethylic acetoacetate or ethylic malonate.

Dehydracetic acid does not give an acetyl derivative, but when treated with phenylhydrazine, or hydroxylamine, the ordinary reaction occurs which takes place when a carboxyl group is present.

With pentachloride of phosphorus, it gives a dichloride, two hydroxyl groups being replaced by chlorine; this reaction at first sight seems to contradict the non-formation of an acetyl derivative, but in all probability it can be explained by the peculiar nature of the acid, as it contains the residues of two ethylic acetoacetate molecules, and it is quite conceivable that, as in the case of ethylic acetoacetate, the following reaction takes place:—

$$-CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2- \text{ gives } -CCl_2{\cdot}CH_2{\cdot}CCl_2{\cdot}CH_2-,$$

and then hydrochloric acid splitting away the group

$$-CCl{:}CH{\cdot}CCl{:}CH-$$

would remain.

On warming with alkalis, a complete decomposition of the molecule takes place, and the same products are obtained as when ethylic acetoacetate is treated in a similar manner.

Dehydracetic acid yields pyridine derivatives with great ease when heated with ammonia, but this is probably due to a partial rearrangement of the molecule after the addition of the elements of water and the subsequent elimination of carbon dioxide.

Most of the methods of formation and also of the decompositions of the dehydracetic acid are well explained by Feist's formula; for instance, the decomposition, when boiled with alkalis, which yields a carbonate and acetate of the alkali and acetone,

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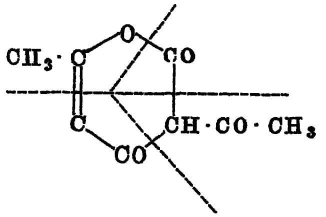
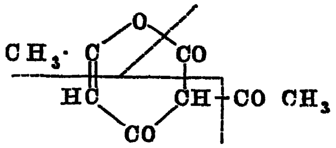
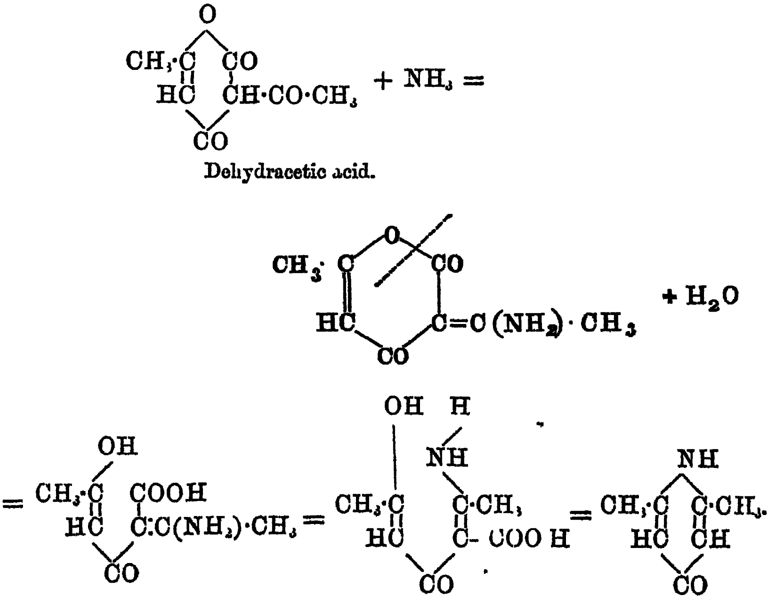
* Ostwald, "Über die Affinitätsgrössen organischen Saüren und ihrer Beziehung zur Zuzammensetzung und constitution derselben." Leipzig, 1889.



or



and by an ingenious reaction, the formation of the pyridine derivative, lutidone, where the two methyl groups are in the $\alpha\alpha'$-position, is also accounted for.

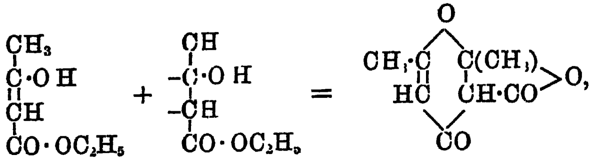


Dehydracetic acid.

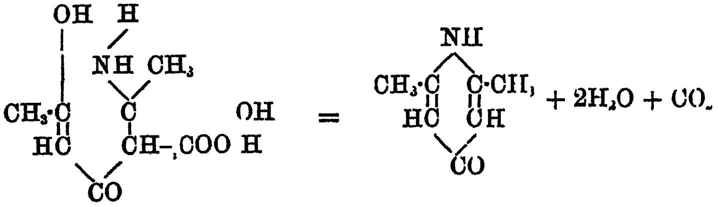
Lutidone.

When we come to the production of a dichloride, where apparently two hydroxyl groups are replaced by chlorine, we at once perceive the inadequacy of the "*wahre Constitutions-formel.*" The production of orcinol and the formation of a methylic ether possessing acid properties are also not easy of explanation. The expression made use of by Feist "währe Constitutions-formel" may be regarded in the light of a challenge to other chemists to devise a formula better adapted to express all the changes which take place during the formation and decompositions of dehydracetic acid; and the considerations which follow *per se*. I venture to think that the last has not been said on the subject.

There are two formulæ which might possibly be preferable to Feist's. The first, in which the two methyl groups are in the $\alpha\alpha'$-position, thus—



and where, instead of alcohol being eliminated in the δ-lactone position, the β-position is used. The production of lutidone would by this formula be as follows:—



It is probable, however, that if this were the case, the formula for dehydracetic acid would be $C_{16}H_{16}O_8$, as it would belong to the class of lactides. This is not so, as a determination of its molecular weight by Raoult's method gave the following result:—

0·600 gram substance lowered the m p of 35·05 grams acetic acid 0·40° C.

	Found.	Calculated for $C_8H_8O_4$.
Mol. weight............	167	168

But the formula which I next propose still more satisfactorily explains the reactions of dehydracetic acid, and not only accounts for these reactions of dehydracetic acid where Feist's formula fails, but also throws additional light on the formation and constitution of many other substances as well as dehydracetic acid.

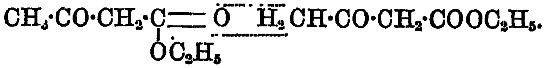
It is well known that the acetyl group easily reacts in the following way:—

$$CH_3{\cdot}C{:}O \quad H_2CH{\cdot}CO,$$

as in the formation of mesityl oxide and mesitylene,

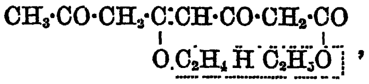
$$(CH_3)_2C{:}O \quad H_2CH{\cdot}CO{\cdot}CH_3;$$

cinnamic acid from benzaldehyde and acetic acid, and in many other cases when the methyl group is attached to an electro-negative group. If we apply this to acetoacetic ether, we get the following reaction :—



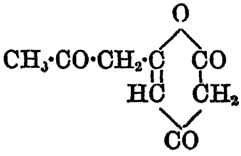
$$CH_3\cdot CO\cdot CH_2\cdot \underset{OC_2H_5}{C}{=}O \;\; H_2\,CH\cdot CO\cdot CH_2\cdot COOC_2H_5.$$

But alcohol and ethylene are also produced during the preparation of dehydracetic acid,



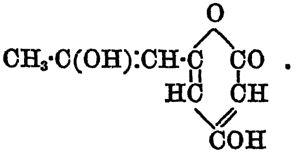
$$CH_3\cdot CO\cdot CH_2\cdot \underset{O.C_2H_4\,H}{C}:CH\cdot CO\cdot CH_2\cdot \underset{C_2H_5O}{CO},$$

and the substance remaining is therefore a δ-lactone, which can be written—



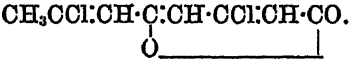
Dehydracetic acid.

or



Tautomeric form.

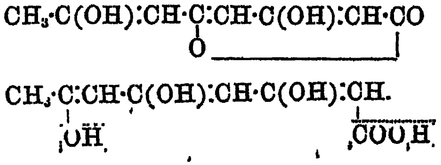
We see now that dehydracetic acid contains two hydroxyl groups; hence it will react with pentachloride of phosphorus, giving



$$CH_3CCl:CH\cdot \underset{O}{C}:CH\cdot CCl:CH\cdot CO.$$

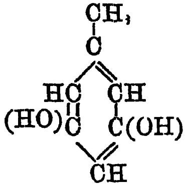
The replacement of the hydrogen of one hydroxyl group by methyl still leaves another hydroxyl group which can react with sodium, yielding a sodium compound; and if the acid property of dehydracetic acid is due to the presence of these groups, the monomethyl ether would probably possess acid properties. This, however, is not to be insisted on, as the acid reaction of dehydracetic acid may quite possibly be due to the presence of the methylene groups which are placed between the carbonyl groups.

The formation of orcinol by heating the acid with baryta-water also follows easily :—



$$CH_3\cdot C(OH):CH\cdot \underset{O}{C}:CH\cdot C(OH):CH\cdot CO$$

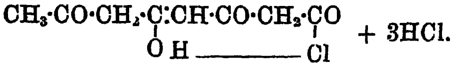
$$CH_3\cdot \underset{OH}{C}:CH\cdot C(OH):CH\cdot C(OH):\underset{COOH}{CH}.$$



Orcinol.

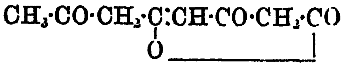
The production of dehydracetic acid from chloride of acetyl by heating it with pyridine is also easy to understand:—

$$\mathrm{CH_3{\cdot}CO\,Cl \quad H\,CH_2{\cdot}CO\,Cl \quad H\,CH_2{\cdot}CO\,Cl \quad H\,CH_2{\cdot}COCl} =$$



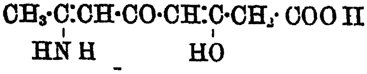
$$\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}\underset{O\,H}{C}{:}CH{\cdot}CO{\cdot}CH_2{\cdot}\underset{Cl}{CO}} + 3HCl.$$

The formation of lutidone is also accounted for by the elimination of water from the δ-lactone position—

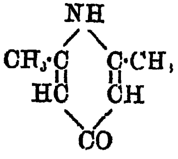


$$\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}\underset{O}{C}{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO}$$

with ammonia and water gives—

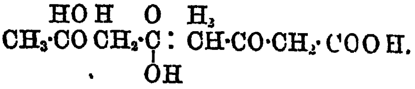


$$\mathrm{CH_3{\cdot}\underset{HN\,H}{C}{:}CH{\cdot}CO{\cdot}CH{:}\underset{HO}{C}{\cdot}CH_2{\cdot}\,COO\,H}$$



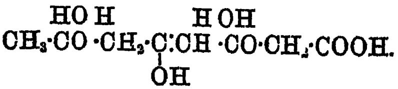
Lutidone.

Dehydracetic acid, when boiled with alkalis, yields acetic acid, acetone, and carbonic acid:—



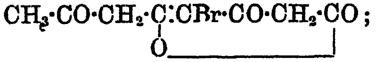
$$\mathrm{\overset{HO\,H}{CH_3{\cdot}CO\,CH_2}{\cdot}\underset{OH}{\overset{O}{C}}:\overset{H_2}{CH}{\cdot}CO{\cdot}CH_2{\cdot}\,COO\,H.}$$

Malonic acid is also sometimes produced:—



$$\mathrm{\overset{HO\,H}{CH_3{\cdot}CO}\,{\cdot}CH_2{\cdot}\underset{OH}{C}{:}\overset{H\,OH}{CH}\,{\cdot}CO{\cdot}CH_2{\cdot}COOH.}$$

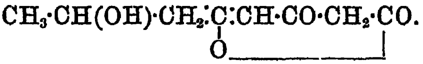
The bromine derivative would have the following formula:—



$$\begin{array}{l}\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}C{:}CBr{\cdot}CO{\cdot}CH_2{\cdot}CO;}\\ \qquad\qquad\qquad\ \ \mathrm{O}\underline{\qquad\qquad\qquad\quad}|\end{array}$$

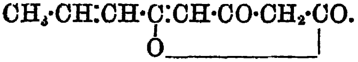
and the compounds produced by the action of nascent hydrogen are—

$C_8H_{10}O_4$



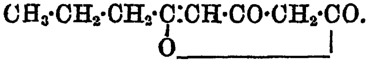
$$\begin{array}{l}\mathrm{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}C{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO.}\\ \qquad\qquad\qquad\qquad\qquad\ \ \mathrm{O}\underline{\qquad\qquad\qquad\quad}|\end{array}$$

$C_6H_8O_3$



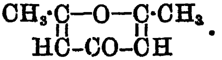
$$\begin{array}{l}\mathrm{CH_3{\cdot}CH{:}CH{\cdot}C{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO.}\\ \qquad\qquad\qquad\ \ \mathrm{O}\underline{\qquad\qquad\qquad\quad}|\end{array}$$

$C_8H_{10}O_3$



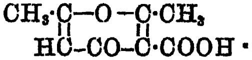
$$\begin{array}{l}\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO.}\\ \qquad\qquad\qquad\quad\ \ \mathrm{O}\underline{\qquad\qquad\qquad\quad}|\end{array}$$

Feist, by heating dehydracetic acid with hydriodic acid in a sealed tube, converted it into the $\alpha\alpha'$-dimethylpyrone,



$$\begin{array}{l}\mathrm{CH_3{\cdot}C{-}O{-}C{\cdot}CH_3}\\ \qquad\ \|\qquad\ \ \|\\ \qquad\mathrm{HC{-}CO{-}CH}\end{array}.$$

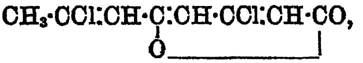
This substance he also produced by heating an acid that he obtained by the action of sulphuric acid on the dichloride. This acid is isomeric with dehydracetic acid. The measurements of its conductivity by Oswald show that it evidently contains a carboxyl group, and Feist calls it the "*währe Dimethylpyrone-carbonsaure*," and gives it the following constitution:—



$$\begin{array}{l}\mathrm{CH_3{\cdot}C{-}O{-}C{\cdot}CH_3}\\ \qquad\ \|\qquad\ \ \|\\ \qquad\mathrm{HC{-}CO{-}C{\cdot}COOH}\end{array}\cdot$$

This is the formula originally suggested for dehydracetic acid by Perkin.

If, however, the formula for the dichloride be

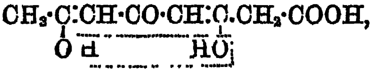


$$\begin{array}{l}\mathrm{CH_3{\cdot}CCl{:}CH{\cdot}C{:}CH{\cdot}CCl{:}CH{\cdot}CO,}\\ \qquad\qquad\qquad\ \ \mathrm{O}\underline{\qquad\qquad\qquad\quad}|\end{array}$$

then, by elimination of hydrogen chloride and the addition of the elements of water, we get—

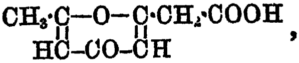
$$\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH,}$$

or



$$\begin{array}{l}\mathrm{CH_3{\cdot}C{:}CH{\cdot}CO{\cdot}CH{:}C.CH_2{\cdot}COOH,}\\ \qquad\quad\ \mathrm{O\ H}\cdots\cdots\cdots\mathrm{HO}\end{array}$$

and Feist's dimethylpyronecarboxylic acid becomes—

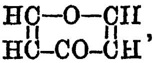


$$\begin{array}{l}\mathrm{CH_3{\cdot}C{-}O{-}C{\cdot}CH_2{\cdot}COOH} \\ \quad\;\mathrm{HC{-}CO{-}CH}\end{array},$$

α-Methylpyroneacetic acid.

which on heating would lose carbon dioxide and give αα′-dimethylpyrone; the true dimethylcarboxylic acid has therefore yet to be produced.

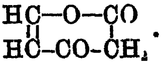
If therefore the formula which I have given to dehydracetic acid be the correct one, it is not a derivative of pyrone,



$$\begin{array}{l}\mathrm{HC{-}O{-}CH} \\ \mathrm{HC{-}CO{-}CH}\end{array},$$

Pyrone.

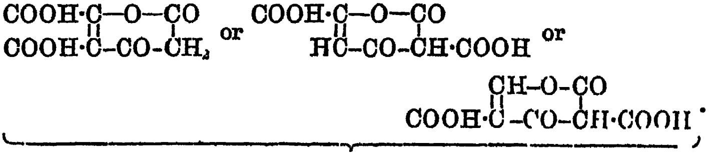
as Perkin suggested in his paper (Trans., 1887, 489), but of oxypyrone, or the δ-lactone of β-oxyacrylylacetic acid,



$$\begin{array}{l}\mathrm{HC{-}O{-}CO} \\ \mathrm{HC{-}CO{-}CH_2}\end{array}.$$

α-Oxypyrone.

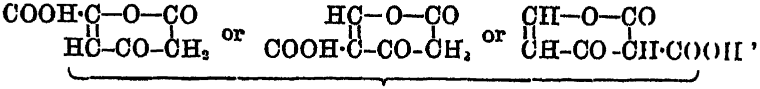
The compounds meconic acid, comenic acid, and pyromeconic acid, which seem to be connected with pyrone or oxypyrone, might possibly have the following formulæ, thus—



$$\underbrace{\begin{array}{l}\mathrm{COOH{\cdot}C{-}O{-}CO} \\ \mathrm{COOH{\cdot}C{-}CO{-}CH_2}\end{array}\ \text{or}\ \begin{array}{l}\mathrm{COOH{\cdot}C{-}O{-}CO} \\ \qquad\mathrm{HC{-}CO{-}CH{\cdot}COOH}\end{array}\ \text{or}\ \begin{array}{l}\qquad\quad\mathrm{CH{-}O{-}CO} \\ \mathrm{COOH{\cdot}C{-}CO{-}CH{\cdot}COOH}\end{array}}.$$

Meconic acid.

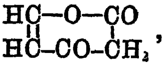
Comenic acid, which is formed by the elimination of carbon dioxide from meconic acid by heat, would be—



$$\underbrace{\begin{array}{l}\mathrm{COOH{\cdot}C{-}O{-}CO} \\ \qquad\mathrm{HC{-}CO{-}CH_2}\end{array}\ \text{or}\ \begin{array}{l}\qquad\quad\mathrm{HC{-}O{-}CO} \\ \mathrm{COOH{\cdot}C{-}CO{-}CH_2}\end{array}\ \text{or}\ \begin{array}{l}\mathrm{CH{-}O{-}CO} \\ \mathrm{CH{-}CO{-}CH{\cdot}COOH}\end{array}},$$

Coumenic acid.

and pyromeconic could only be—

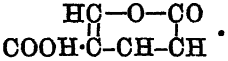


$$\begin{array}{l}\mathrm{HC{-}O{-}CO} \\ \mathrm{HC{-}CO{-}CH_2}\end{array},$$

Pyromeconic acid.

or the δ-lactone of β-oxyacrylylacetic acid.

Coumalinic acid, as Pechmann and Welsh have shown (Trans., 1885, **47**, 149), also probably belongs to this δ-lactone class—

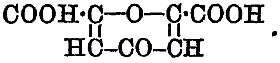


$$\begin{array}{r}\mathrm{HC{-}O{-}CO} \\ \mathrm{COOH{\cdot}C{-}CH{-}CH}\end{array}.$$

Coumalinic acid.

The decomposition which these meconic acid compounds undergo when boiled with alkalis, acetone being formed, can now be easily understood.

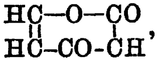
Closely connected with these oxypyrone compounds are the true pyrone compounds, to which class chelidonic acid no doubt belongs—



$$\begin{array}{c}\mathrm{COOH{\cdot}C{-}O{-}C{\cdot}COOH} \\ \mathrm{HC{-}CO{-}CH}\end{array}.$$

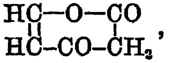
Chelidonic acid.

There probably also exists an analogous series of compounds, containing a carbonyl group fewer than pyrone and oxypyrone derivatives; this series is the furfuran and oxyfurfuran class:—



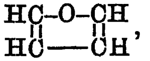
$$\begin{array}{l}\mathrm{HC{-}O{-}CO} \\ \mathrm{HC{-}CO{-}CH}\end{array},$$

Pyrone.



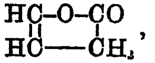
$$\begin{array}{l}\mathrm{HC{-}O{-}CO} \\ \mathrm{HC{-}CO{-}CH_2}\end{array},$$

Oxypyrone.



$$\begin{array}{l}\mathrm{HC{-}O{-}CH} \\ \mathrm{HC{-\!-}CH}\end{array},$$

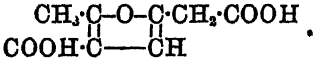
Furfuran.



$$\begin{array}{l}\mathrm{HC{-}O{-}CO} \\ \mathrm{HC{-\!-}CH_2}\end{array},$$

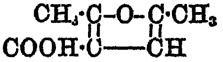
Oxyfurfuran.

and as ammonia gives pyridine derivatives with the one class, so it should yield pyrrolene derivatives with the other. Several instances might be given of the furfuran compounds, thus—



$$\begin{array}{r}\mathrm{CH_3{\cdot}C{-}O{-}C{\cdot}CH_2{\cdot}COOH} \\ \mathrm{COOH{\cdot}C{-\!-}CH\phantom{{\cdot}CH_2{\cdot}COOH}}\end{array}.$$

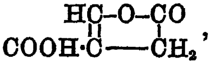
Methronic acid.



$$\begin{array}{r}\mathrm{CH_3{\cdot}C{-}O{-}C{\cdot}CH_3} \\ \mathrm{COOH{\cdot}C{-\!-}CH\phantom{{\cdot}CH_3}}\end{array}$$

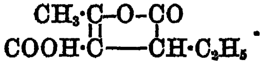
Uvic acid.

and to the oxyfurfuran class belong aconic acid and the ketolactonic acid of Young (*Annalen*, **216**, 45),



$$\begin{array}{r}\mathrm{HC{-}O{-}CO} \\ \mathrm{COOH{\cdot}C{-\!-}CH_2}\end{array},$$

Aconic acid.

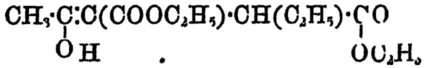


$$\begin{array}{l}\mathrm{CH_3{\cdot}C{-}O{-}CO} \\ \mathrm{COOH{\cdot}C{-\!-}CH{\cdot}C_2H_5}\end{array}.$$

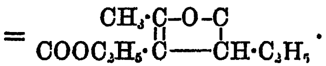
Ketolactonic acid.

The production of the ketolactonic acid is of some interest, as it is formed in small quantities during the distillation of ethylic β-ethylacetosuccinate, in the same manner as dehydracetic acid is produced from ethylic acetoacetate—

$$CH_3{\cdot}CO{\cdot}CH(COOC_2H_5){\cdot}CH(C_2H_5){\cdot}COO(C_2H_5),$$

or 

$$\underset{OH}{CH_3{\cdot}C}{:}C(COOC_2H_5){\cdot}CH(C_2H_5){\cdot}\underset{OC_2H_5}{CO}\ .$$



$$= \begin{array}{l}CH_3{\cdot}C{-}O{-}C\\ COOC_2H_5{\cdot}C{-\!\!-}CH{\cdot}C_2H_5\end{array}.$$

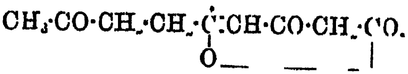
It is hardly necessary to point out the fact that if the above be the correct explanation of the production of dehydracetic acid from ethylic acetoacetate, then dehydrobenzoylacetic acid must be formed by another reaction, as it does not contain a methyl group. That this is so is rendered possible by the reactions of dehydrobenzoylacetic acid, notably the action of pentachloride of phosphorus; and the formula suggested by Feist (*Ber.*, **18**, 3726) may be the correct one

Closely connected with dehydracetic acid is the dihydrodiacetyllævulinic acid of Magnanini (*Gazzetta*, **19**, 275); it is, in all probability, the next higher homologue of the dehydracetic acid series—

$C_4H_6O_3$ Acetoacetic acid.	$C_8H_8O_4$. Dehydracetic acid.	C_7H_9NO. Lutidone.
$C_5H_8O_3$. Lævulinic acid.	$C_9H_{10}O_4$. Dehydrodiacetyl-lævulinic acid.	$C_8H_{11}NO$. α Methyl-α-acetonyl-pyrrolene

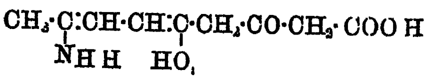
It was obtained by heating lævulinic acid to a very high temperature with acetic anhydride. It easily yields, with ammonia, a compound which has the formula $C_8H_{11}NO$, which in its turn gives, when heated with zinc-dust, pyrrolene, and not *pyridine*.

The δ-lactone formula for dehydracetic acid shows at once how this is possible—

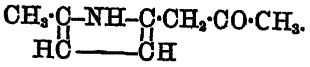


$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{O}{C}{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO.$$

Dehydrodiacetyllævulinic acid.



$$CH_3{\cdot}\underset{NH\,H}{C}{:}CH{\cdot}CH{:}\underset{HO}{C}{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH$$

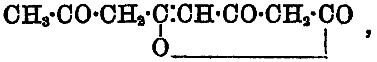


$$\begin{array}{l}CH_3{\cdot}C{-}NH{-}C{\cdot}CH_2{\cdot}CO{\cdot}CH_3.\\ \quad HC{-\!\!-\!\!-}CH\end{array}$$

α-Methyl-α-acetonylpyrrolene.

In this case, by the action of ammonia on the acid, together with water, there is *no hydroxyl group in the δ-position to the nitrogen atom;*

consequently *a γ-imido- or pyrrolene compound is formed.* If then dehydracetic acid is the δ-lactone of the formula—



$$\begin{array}{l} CH_3\cdot CO\cdot CH_2\cdot C{:}CH\cdot CO\cdot CH_2\cdot CO \\ \qquad\qquad\qquad\quad \underline{O\qquad\qquad\qquad\quad |} \end{array},$$

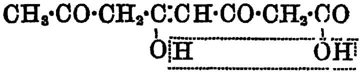
it is probably formed by the condensation of 4 mols. of acetic acid, as Geuther first suggested in 1866, when he gave it the name dehydracetic acid—

$$4C_2H_4O_2 = C_8H_8O_4 + 4H_2O,$$

or

$$CH_3\cdot CO\boxed{OH\quad H}CH_2\cdot CO\boxed{OH\quad H}CH_2\cdot CO\boxed{OH\quad H}CH_2\cdot COOH,$$

then



$$\begin{array}{l} CH_3\cdot CO\cdot CH_2\cdot C{:}CH\cdot CO\cdot CH_2\cdot CO \\ \qquad\qquad\qquad\quad O\boxed{H\qquad\qquad\quad OH} \end{array}$$

and it is the δ-lactone of *tetracetic acid;* and the following list shows the connection between the condensed acids of acetic acid—

$CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot COOH.$
Tetracetic acid.

$CH_3\cdot CO\cdot CH_2\cdot CO.CH_2\cdot COOH.$
Triacetic acid.

$CH_3\cdot CO\cdot CH_2\cdot COOH.$
Diacetic acid.

$CH_3\cdot COOH.$
Acetic acid.

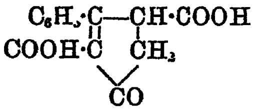
But the tri- and tetra-acids would of course yield at once δ-lactones.

Up to the present time, triacetic acid does not seem to have been obtained, unless the carbacetic acid of Duisberg, $C_6H_6O_3$, be identical with its lactone. The ethyl ether of this acid was obtained by allowing a solution of hydrogen chloride in ethylic acetoacetate to stand for four weeks.

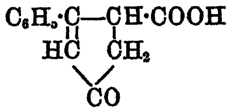
XXI.—*Phenuvic Acid; Contributions to our knowledge of its Constitution, and Relationship with the Phenylmethylfurfurancarboxylic Acid of Paal.*

By Arthur Colefax, B.A., Ph.D., late Natural Science Postmaster of Merton College, Oxford.

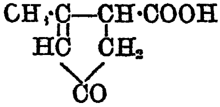
By the condensation of ethyl benzoylacetate and sodium succinate in the presence of acetic anhydride, Schloesser (*Annalen*, **250**, 212) obtained an ethyl salt of a bibasic acid, which, at the suggestion of Professor Fittig, he named phenythronic acid. This acid is the aromatic representative of methronic acid, an acid which, as its discoverer, v. Eyern, showed, gives, by elimination of 1 mol. of carbonic acid, Harrow's pyrotritartaric acid (*Annalen*, **201**, 141). Corresponding to the alternative name "uvic acid" for the acid of Harrow, Fittig suggested the name phenuvic acid for Schloesser's monobasic acid. Fittig interprets the constitution of the acids referred to above, as follows:—



Phenythronic acid.

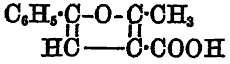


$C_{12}H_{10}O_3$, phenuvic acid.

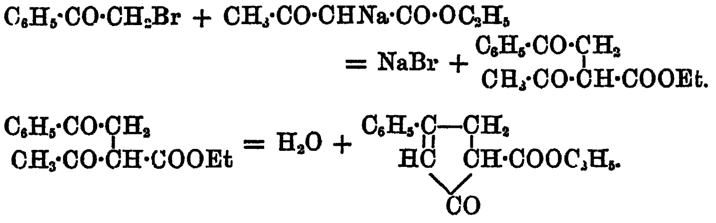


Pyrotritartaric (uvic) acid.

Paal (*Ber.*, **16**, 2865), by the action of the sodium compound of ethyl acetoacetate upon bromacetophenone, obtained an ether which, by subsequent splitting off of the elements of water, yielded the ether of an acid which he regarded as phenylmethylfurfurancarboxylic acid. To this compound, Paal gave, therefore, the constitution



Fittig did not accept this constitution for Paal's acid, but, regarding it as an isomer of phenuvic acid, assigned to it an analogous formula, and interpreted Paal's reaction as follows:—



$$C_6H_5{\cdot}CO{\cdot}CH_2Br + CH_3{\cdot}CO{\cdot}CHNa{\cdot}CO{\cdot}OC_2H_5 = NaBr + \begin{array}{l} C_6H_5{\cdot}CO{\cdot}CH_2 \\ CH_3{\cdot}CO{\cdot}CH{\cdot}COOEt. \end{array}$$

If the relationship between the acids of Paal and of Schloesser be such as Fittig suggests, whether they possess the constitution assigned to them by Paal or the one accepted by Fittig, a method analogous to the one by which Paal prepared his acid should yield Schloesser's acid. Accordingly, chloracetone reacting with the sodium compound of ethyl benzoylacetate should yield Schloesser's acid by subsequent elimination of the elements of water and saponification of the resulting ether.

At the suggestion of Professor Fittig, I undertook the examination of the reaction between chloracetone and the sodium compound of ethyl benzoylacetate.

In the preparation of the sodium compound of ethyl benzoylacetate, 3·6 grams of sodium, carefully freed from adhering oil, were dissolved in alcohol, in a flask provided with a reflux condenser closed by a calcium chloride tube. The alcohol used had been distilled over lime, and then rendered absolute by further distillation over sodium. To the cold alcoholic solution of sodium ethylate, 30 grams of ethyl benzoylacetate, boiling between 168° and 172° under a pressure of 20 mm. (comp. Claissen, *Ber.*, **20**, 651), were added drop by drop with vigorous shaking. After the addition of the ether was complete, the mixture was gently heated on the water-bath until the alcohol began to distil. The theoretical quantity of pure chloracetone, 14·4 grams, was added drop by drop to the alcoholic solution of ethyl sodium benzoylacetate. No rise of temperature was noticeable, but the separation of sodium chloride proceeded in the cold. Half-an-hour's gentle heating on the water-bath facilitated the reaction, an increased precipitation of sodium chloride being noticed. Finally, the alcohol was evaporated, and the ethyl salt separated by water, and shaken out with ether. The product thus obtained was heated with dilute hydrochloric acid (1 vol. HCl : 4 vols. H_2O) for about an hour, and then distilled with steam. With the exception of a certain quantity of resinous matter which was formed, everything passed over with the steam. The distillate was clearly divisible into two portions,

A. A portion, something like 90 per cent. of the whole, distilling very rapidly, and having the odour of acetophenone.

B. A second fraction continuing to distil during many hours, and developing a phenolic odour.

Each of the fractions of the distillate with steam was shaken out with ether, and then, after the evaporation of the ether, gently warmed with alcoholic potash. After the alcohol had been all got rid of on the water-bath, water was added, and in each case the solution was distilled with steam. In the case of both fractions, there remained something volatile with steam. Fraction A seemed to have been wholly unattacked by the alcoholic potash, and as a result of twice fractionating the product of the second distillation with steam, a sample of pure acetophenone was obtained, which gave on analysis—

	Theory for C_8H_8O.	Found.
C	6·66	6·71
H	80·00	79·59

The portion still volatile in steam after heating fraction B with alcoholic potash was found to distil between 235° and 240°. This, on cooling in a freezing mixture, gave crystals which, when purified by pressing between filter paper, were found to melt at 38 5—39°, and were found to be identical with the neutral compound obtained by Schloesser from his acid (phenuvic acid) by elimination of carbonic anhydride.

To the aqueous solutions, after separation of everything volatile with steam, hydrochloric acid was added to a neutral or only slightly alkaline reaction, and, after decolorising with animal charcoal, were concentrated by evaporation. More hydrochloric acid was then added, with the result that, in the aqueous solution obtained from fraction B, a precipitate was formed, which, on recrystallisation from alcohol, and careful drying over sulphuric acid in a vacuum, gave on analysis—

	Theory for $C_{12}H_{10}O_3$.	Found.
C	4·95	5·05
H	71·29	71·07

From the mother liquor from which the above acid had been precipitated, a crop of crystals of benzoic acid was deposited, after several days' standing in the air. These melted at 119—120°, and the calcium salt gave on analysis :—

0·3128 gram substance gave 0·0510 gram H_2O and 0·1300 gram $CaSO_4$.

	Theory for $(C_6H_5{\cdot}COO)_2Ca,3H_2O$.	Found.
H_2O	16·10	15·84
Ca.............	11·90	11·88

As a result, then, of heating the product of the reaction of chloracetone and ethyl sodium benzoylacetate with dilute hydrochloric acid, there is formed:—

(*a*.) Acetophenone in very large quantities.
(*b*.) An ethereal salt of an acid of the composition $C_{12}H_{10}O_3$.
(*c*.) Small quantities of a neutral compound melting at 38·5—39°.

In addition, we find crystallising out of the mother liquid from which the acid of the composition $C_{12}H_{10}O_3$ has been precipitated, benzoic acid.

Comparison of the Acid $C_{12}H_{10}O_3$ *with Schloesser's Phenuvic Acid.*

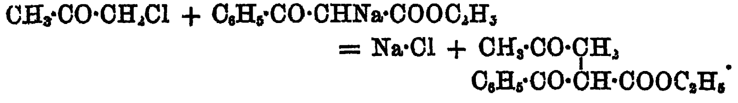
The melting point of a portion of the acid which had been recrystallised from alcohol was taken, and found to lie between the temperatures 144 and 145°. Schloesser gives as the melting point of this acid also the temperature of 144—145°. Moreover, a portion of the acid actually prepared by Schloesser and some of the acid I had obtained were compared, one and the same thermometer being used in both cases, and both were found to melt at precisely the same temperature, 144—145°.

The calcium salt was prepared, and its aqueous solution crystallised by allowing it to evaporate over sulphuric acid in a vacuum. The air-dried salt gave on analysis—

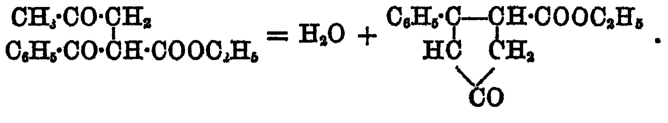
	Theory for $Ca(C_{12}H_9O_3)_2,2H_2O$.	Found.
Ca	7·53	7·54
H_2O	9·05	8·95

The salt was found to be equally soluble in hot and cold water. It lost all its water of crystallisation at 160°. Hence, the acid obtained as a result of the action of chloracetone on ethyl sodium benzoylacetate, by subsequent elimination of the elements of water and saponification of the resulting ether, is identical with phenuvic acid.

Its method of formation, accepting Fittig's formula, may be thus explained:—



$$CH_3{\cdot}CO{\cdot}CH_2Cl + C_6H_5{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 = Na{\cdot}Cl + \begin{array}{l} CH_3{\cdot}CO{\cdot}CH_2 \\ C_6H_5{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5 \end{array}.$$



$$\begin{array}{l} CH_3{\cdot}CO{\cdot}CH_2 \\ C_6H_5{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5 \end{array} = H_2O + \begin{array}{c} C_6H_5{\cdot}C\text{—}CH{\cdot}COOC_2H_5 \\ HC \quad CH_2 \\ CO \end{array}.$$

Further, Paal's acid, phenylmethylfurfurancarboxylic acid, and phenuvic acid are, as Fittig (*Ber.*, **21**, 2135) suggested, isomeric.

Identity of the Neutral Compounds formed from Phenuvic and Phenylmethylfurfurancarboxylic Acids.

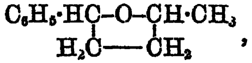
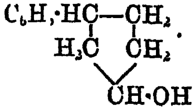
From a comparison of the properties of the compound obtained from phenuvic acid by elimination of carbon dioxide, with those of the compound described by Paal (*Ber.*, **17**, 915 and 2759) as phenylmethylfurfuran, the two would seem to be identical. Specimens of the two were prepared, and found to be identical in every respect. The melting point determinations were found to give the following results:—

The neutral compound from phenuvic acid, called by Fittig phenylketopentene, melted at 38·5—39°; that from Paal's acid, phenylmethylfurfuran, also melted at 38·5—39°. A portion of the product from phenuvic acid caused to crystallise from its solution by the addition of a crystal of the second neutral compound possessed exactly the same melting point. The boiling point of both substances was found to be 241°. The identity of these two compounds is in exact accordance with the isomerism of phenuvic and methylphenylfurfurancarboxylic acids.

Constitution of Phenuvic Acid.

In view of the interesting work of Perkin and Schloesser (Trans., 1890, **57**, 948) on diphenylfurfuran, and the conclusion they draw from it respecting the formula of carbuvic acid and uvic acid, it may be well to detail a few experiments made in the hope of gaining further knowledge of the constitution of phenuvic acid, and to summarise the evidence so far accumulated in support of each of the two formulæ for phenuvic acid and allied compounds.

Tetrahydromethylphenylfurfuran.—This was originally discovered by Paal (*Ber.*, **17**, 2756), who analysed it, and stated that it could be distilled over sodium without decomposition. The formulæ for a tetrahydro-derivative, according as we adopt Paal's formula or Fittig's for the neutral compound, would be—


,

.

With the constitution assigned by Fittig to the neutral substance, we should expect a tetrahydro-derivative to be capable of existence only when endowed with alcoholic properties; whereas, if the constitution proposed by Paal be correct, a tetrahydro-derivative might exist, and still be capable of being distilled over sodium without decomposition.

In view of the theoretical importance of this compound, it was prepared as described by Paal, and some of its properties more fully investigated. 10 grams of the neutral compound were dissolved in about 250 c.c. of alcohol, and treated with 23 grams of sodium; this amount of sodium was four times the quantity theoretically necessary for the production of a tetrahydro-derivative. The sodium, after having been weighed, was kept in absolute ether until required, and was added very gradually. The product, after separating the alcohol, was treated with dilute hydrochloric acid until slightly acid, and then agitated with ether; after evaporating the ether, the residue was distilled with steam (to free it from small quantities of resinous matter), taken up with ether, and eventually fractionated. As a result of three fractionations, it was found possible to obtain a portion (2 grams) boiling constantly at 233°. This was analysed with the following results:—

	Theory for $C_{11}H_{14}O$.	Found. I.	Found. II.
H	8·64	8·90	9·00
C	81·48	81·59	81·43

Action of Sodium on the Neutral Compound.—Paal having stated that the compound could be distilled from sodium without change, it was determined to examine its behaviour towards sodium more fully. In fractionating it over sodium, it was found that in every case the sodium was attacked.

A small quantity, about 0 5 of a gram, was placed in a perfectly dry, small, narrow test tube. The tube was closed with a well-fitting cork, through which passed a thin glass tube, finely drawn out at the end. A small pellet of sodium was introduced, and the tube heated in a sulphuric acid bath. The sodium was immediately attacked, and at 50° the evolution of gas had become tolerably energetic. The liquid became dark brown, and a dark-brown solid separated, which finally stopped the action of the sodium. An exactly similar experiment was tried with the neutral compound, but no trace of gas was noticeable, and the substance remained quite unacted upon.

Attempts to obtain from the tetrahydro-derivative an ether by the action of benzoyl chloride on the sodium compound formed, as in the experiment described above, were unsuccessful. An attempt to obtain an ether by heating the hydrogen compound with acetic anhydride was also attended with no better success.

Action of Benzoyl Chloride.—0·5 gram of the hydrogen compound was then heated with benzoyl chloride. The experiment was made exactly as in the case where the action of sodium was examined, except that the finely drawn out tube was bent downwards. At 35°, the liquid assumed a light-green tint, which darkened as the temperature rose, and finally became dark brown. At 110°, the evolution of hydrogen chloride was marked, and only ceased after the lapse of half-an-hour. This temperature was maintained for another hour, and on subsequently raising the temperature to 145°, no further evolution of hydrogen chloride took place. The benzoyl chloride, the excess of which was removed by long-continued shaking with sodium carbonate solution, was used in quantities slightly in excess of the theoretical, assuming the hydrogen compound to be an alcohol. It had been freshly distilled, and had a constant boiling point.

The following experiments were made with the liquid product:—A portion was boiled with a solution of pure sodium carbonate, and after removal of the still remaining oil, the solution was tested for chlorine. Traces only were found, and on acidifying the solution no benzoic acid was precipitated. A second portion was heated with caustic potash. After removing the oil still remaining, and then acidifying, an abundant precipitation of benzoic acid took place. An analysis made with a view to determine the percentage of the benzoyl radicle in it, gave 23·32 per cent. $C_6H_5 \cdot CO$, instead of 39·47 per cent., the theoretical amount if the substance was pure benzoic ether.

It may be that benzoyl chloride, in addition to forming an ether, causes the elimination of water from the hydrogen compound, and this may be the reason of the impurity of the product obtained from the action between these two substances.

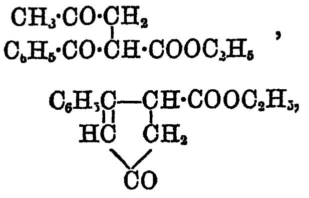
Attempts to obtain from the neutral compound a combination with hydrogen bromide failed. Though the experiment was made at the temperature of ice-cold water, decomposition of the neutral compound occurred, and no addition of hydrogen bromide was accomplished.

Hydrobromic acid was without action on either Paal's acid or on phenuvic acid.

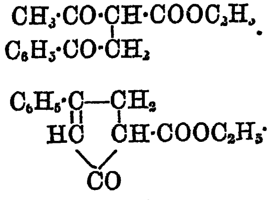
Some of Paal's acid was treated with sodium amalgam, care being taken to avoid the solution becoming too alkaline; on adding hydrochloric acid, the whole of the original acid was recovered, unchanged in appearance, and showing the correct melting point.

Conclusions.

The formation of phenuvic acid from acetophenone ethyl benzoyl acetate, and of phenylmethylfurfurancarboxylic acid from benzophenone ethyl acetoacetate, as explained by Fittig, supposes a methyl grouping to be instrumental in effecting the inner condensation, thus:—

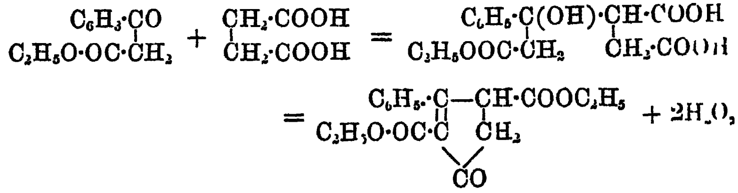


Phenuvic acid.



Paal's acid.

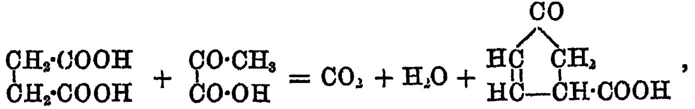
The reaction between ethyl benzoylacetate and sodium succinate is attributed (*Ber.*, **21**, 2133) to a methylene grouping in the succinic acid:—



whereby the diethyl phenythronate results.

As Perkin and Schloesser (*loc. cit.*) point out, the formation of diphenylfurfuran derivatives from dibenzoylsuccinate precludes the possibility of a condensation taking place similar to those just given. Moreover, from the analogy in the internal condensation of dibenzoyl succinate and diacetyl succinate, one seems compelled to admit a similarity in constitution of the resulting compound, and thus to regard carbuvic and uvic acids as furfuran derivatives.

The support Fittig (*Ber.*, **22**, 2104) found for his formula in the condensation taking place between pyruvic acid and sodium succinate, which Parker and Fittig showed gave a compound $C_6H_6O_3$, and whose constitution Fittig explained:—



no longer holds good. Further investigation has proved the original assumption that the compound was a new acid, the parent substance of uvic acid, to be wrong. It is now recognised as the anhydride of pyrocinchonic acid (*Ber.*, **23**, 1535). However, the support which the existence of a tetrahydride, distilling over sodium undecomposed, gave to the furfuran formula must now be laid aside. The compound is attacked by sodium. Moreover, the experiment with benzoyl chloride seems to point to the possibility of obtaining a benzoic ether. The failure of nascent hydrogen to act on Paal's acid is in exact agreement with what v. Eyern found in the case of methronic acid. The bibasic acid dehydromucic acid readily takes up two atoms of hydrogen. Here is a marked difference in the behaviour with nascent hydrogen of compounds supposed to be furfuran derivatives, and of dehydromucic acid, which is a furfuran derivative.

With the evidence that has so far been accumulated, I think it is impossible to reject either formula. I have used Professor Fittig's formula throughout the paper, because it comes most natural to me to regard these compounds in this light, not because of any conviction of their absolute accuracy.

In conclusion, I would say the above work was done in the laboratory of the Kaiser Wilhelm's Universitat, Strassburg, and I would take this opportunity of thanking Professor Fittig for the great kindness he showed me during my student life in Strassburg.

XXII.—*Magnetic Rotation.*

By W. Ostwald.

Our present knowledge of the relation between the magnetic rotation of chemical compounds and their composition and constitution is due solely to the work of Dr. W. H. Perkin, who, by his patient and searching investigations, has made it possible to establish general relations in this branch of science, more particularly among the organic compounds. One of the general results of this work is the conclusion that the magnetic rotation is an additive property, that is, that the magnetic rotation of a compound is the sum of the magnetic rotations of its components.

But this additive character of the molecular rotation only exists as a rough approximation, and more precisely only among members of the same homologous series of organic compounds. Such slight differences as the transition from a compound to one of its isomerides causes perceptible alterations in the rotation. Dr. Perkin has taken these influences into consideration in the determination of his "series-constants," to which he gives values which depend on the chemical character of each series, whilst the increase in the magnetic rotation caused by the addition of a CH_2 group is the same in all the different series.

These facts may be expressed by the statement that the magnetic rotation is in the first instance an additive property, but is subject to influences of a constitutive character. For doubtless the observed differences depend on those properties which we are accustomed to term differences of constitution.

A similar behaviour characterises most of the other physical properties of matter. A purely additive property is only to be found in the *mass* or weight, the mass of a chemical compound being exactly the sum of the masses of its components. All other properties are affected more or less by the influence of constitution. In the case of the refractive power, this influence is not very great, no great differences existing in the refractive powers of isomerides, but chemical differences like those between saturated and unsaturated compounds are attended by corresponding differences in the refractive power, as shown by the investigations of Gladstone, Brühl, and others. Perfectly similar relations hold also for the molecular volumes.

Other properties, as for instance colour and optical rotation, are of so pronounced a constitutive character, that the additive property almost entirely disappears. In certain cases it is, however, known that a definite alteration in chemical composition is attended by a definite change in the wave-lengths of the absorption bands of different compounds, and hence, the additive character of this property is made evident, although only within narrow limits.

The magnetic rotation occupies a mid-position among the properties above mentioned; it depends in a greater degree on constitution than does the refractive power or the molecular volume, and in a less degree than colour. Its additive character is more pronounced than that of the latter, its dependence on constitution more pronounced than that of the former properties.

Up to the present time, there is a full agreement between all the facts known with regard to the magnetic rotation and our generally adopted views with regard to constitution, as far as organic compounds are concerned. But when we turn to inorganic compounds, we find that this agreement does not exist, and we must therefore conclude that our views respecting the constitution of the latter are in some points erroneous.

Dr Perkin has calculated from his observations on organic chlorides that the atomic rotation of chlorine in these compounds has the value 1·73. Combined hydrogen has the rotation 0·25, and making an allowance of 0·2 for the free state (Trans., 1889, **55**, 739), the molecular rotation of hydrogen chloride must be approximately 2·18. A solution of this compound in isoamyl oxide gave, as a matter of fact, in accordance with this calculation, 2·24. But in aqueous solution the molecular rotation was found to increase with rising dilution from 4·05 to 4·42. In a similar manner, hydrobromic acid gives 7·67 to 8·52 instead of the calculated value 4·02, and hydriodic acid gives 17·77 to 18·43 instead of 8·21.

In accordance with all general principles, we should have to assign such marked deviations from the laws governing additive properties to some profound change in chemical constitution. Evidence of such a change in the passage from organic to inorganic haloïd compounds does exist. It is well known that whereas the organic chlorides are not precipitated by silver nitrate, the aqueous solutions of the inorganic chlorides are, and that while none of the former conducts electricity, the latter do, and so on. Such great differences as these in behaviour and properties are doubtless connected with corresponding important differences in constitution, and unless our present knowledge is sufficient to give the explanation, it would be necessary to discover the cause of such differences as soon as possible.

In the first instance, it may be asked whether chemical differences similar to the above are in every case attended by similar differences in magnetic rotation. This has been fully answered by Dr. Perkin's last publication. All aqueous solutions of haloïd compounds which are precipitated by silver nitrate and are good electrolytes show the same high values in magnetic rotation. We have for example

$NaCl = 5·07$, $KCl = 5·38$, $LiCl = 4·70$, $\frac{1}{2}CaCl_2 = 4·54$.
$\frac{1}{2}MgCl_2 = 4·56$, $NH_4Cl = 6·10$.
$NaBr = 9·03$, $KBr = 9·22$, $NH_4Br = 10·20$.
$NaI = 18·87$, $KI = 18·69$, $NH_4I = 20·00$.

These exceptional values are only found in aqueous solutions, and such aqueous solutions alone are electrolytes. Hydrogen chloride, which, in aqueous solution, is one of the best electrolytes, almost totally loses its conductivity when dissolved in organic solvents (Kablukoff, *Zeit. physikal. Chem.*, 4, 429). Therefore, as Dr. Perkin has found, solutions in a non-aqueous medium alone exhibit the ordinary additive property, the magnetic rotation being simply the sum of the rotations of the solvent and the dissolved substance.

But he has also found that some aqueous solutions exist which possess an additive character. If the above considerations are correct, these solutions cannot be good conductors. And indeed the additive property only occurs in aqueous solutions of indifferent substances such as alcohol, and of weak acids and bases such as acetic, formic, and propionic acids, ammonia and its organic derivatives. All these compounds in aqueous solution are much poorer conductors of electricity than the strong acids and bases, and we must therefore conclude that they only undergo in a very small degree that alteration in constitution which is so marked in the case of the haloïd acids. Since the salts formed from weak acids are as good conductors as those formed from strong ones, we may expect with them also marked deviations from the calculated values. No observations have, up to the present, been made with such bodies; it would be of interest to investigate some of these salts, such as ammonium formate or acetate.

As is well known, within recent times, the fundamental difference between electrolytes and non-electrolytes has been explained by Arrhenius on the theory of electrolytic dissociation. Is it necessary to point out that the facts observed by Dr. Perkin are in full accordance with this much debated theory, and quite inexplicable by any of the older views? In every case in which we must assume with Arrhenius that the compound dissociates into free ions, we find great variations in the magnetic rotation, and *vice versâ*.

The transition of a compound into the state of electrolytic dissociation may be accompanied by an increase in the magnetic rotation, as in the case of the haloïd acids, or also with a decrease. Dr. Perkin formerly (Trans., 1887, 51, 808) investigated sulphuric and nitric acids in the pure state (when they are non-electrolytes) and in aqueous solution (when they are dissociated). The former gave:—

	$\rho.H_2SO_4$.
H_2SO_4	2·32
$H_2SO_4 + H_2O$	2·19
$H_2SO_4 + 2H_2O$	2·11
$H_2SO_4 + 3H_2O$	2·06

Here the magnetic rotation of sulphuric acid decreases with rising dilution, and the same is also true of nitric acid. In organic compounds, both acids have the same values as in the pure and undiluted state, this being in accordance with the fact that these organic compounds are non-electrolytes. A very conclusive fact is the following:— Since the dissociation increases with rising dilution, the difference, positive or negative, between the magnetic rotation of the compound in the dissociated and non-dissociated condition must also increase with rising dilution, that is, the absolute value of the rotation must increase with dilution in the case of the haloïd acids and decrease with sulphuric and nitric acids, as is actually the case. Since the aqueous solutions of the ammonium salts contain these compounds in the state of electrolytic dissociation, the molecular rotations of ammonium nitrate and sulphate must also be less than the calculated values, whilst the haloïd salts of ammonium must give greater values. These conclusions are also confirmed by Dr. Perkin's observations.

It would be possible to point out a number of other instances of the agreement between the Arrhenius theory and Dr. Perkin's observations. But for those who are acquainted with this wonderful theory, the task is a superfluous one, and it would be a useless waste of time to enumerate them in this place. For those unacquainted with the theory, the above explanations will, I hope, be sufficient to induce them to make its acquaintance.

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XXIII.—*Action of Phosphoryl Chloride on Phosphorus Pentoxide.*

By G. N. Huntly, Assoc. R.C.Sc. (Lond.).

In 1871, Gustavson, in a preliminary note (*Ber.*, 4, 853), described the existence of a viscous mass obtained by heating a mixture of phosphoryl trichloride with phosphorus pentoxide in equal molecular proportions at 200° for 36 hours. This substance he regarded as either metaphosphoryl chloride, PO_2Cl. or as a mixture of this substance with its polymers. In this preliminary note, Gustavson made no attempt to prove whether this viscous mass was homogeneous or not. Geuther, in his memoir on the "Mutual Reactions of the Chlorides and Acids of Phosphorus" (*J. pr. Chem.* [2], 8, 359), attempted to prepare this compound by heating metaphosphoric acid with phosphorus pentachloride. He was not able to obtain any compound agreeing with the chloride PO_2Cl, but found phosphoryl trichloride as the only product. More recently, Thorpe and Tutton (Trans., 1890, 57, 572), by the action of chlorine on phosphorous oxide, P_4O_6, obtained phosphoryl trichloride and a viscous substance having the appearance and composition of Gustavson's chloride. As the properties of this singular substance appeared to be worthy of a more extended investigation, I have, at Professor Thorpe's suggestion, undertaken to make a more detailed examination of the compound.

To begin with, I repeated Gustavson's experiment. A mixture of phosphoryl trichloride and phosphorus pentoxide, in equal molecular proportions, was heated in a sealed tube at 200°. After 20 hours heating, the greater part of the phosphorus pentoxide was dissolved, the whole forming a light-brown, viscous mass. But some portions of the oxide remained unaltered, and even after 120 hours at 200—215°, some unattacked pentoxide remained. The composition of this mass is practically given by the proportions of the two substances put into the tube; but since, owing to its peculiar properties, solvents could only be made to act on a small surface, and since it could be neither distilled nor crystallised, it was impossible to decide whether this mass was really one substance or several. It was noticed, however, that it gave off phosphoryl trichloride at 150°, or 50° below the temperature at which it was formed. This showed that the reaction in the tube was reversible, and suggested an increase in the mass of the phosphoryl trichloride relatively to that of the oxide. Hence in later experiments the amount of the trichloride varied from 2 to 4 mols. to 1 of the pentoxide. Under these conditions, on heating at 200°, the phosphorus pentoxide slowly dissolves, the solution being complete in from 40 to 80 hours. Further heating does not appear to affect the properties of this solution. On account of its exceedingly hygroscopic properties, it is best kept in small, sealed glass bulbs.

If the product is distilled* in a small, weighed distillation flask, pure phosphoryl trichloride (b. p. 107°) distils over. The distillation of the oxychloride after a time ceases, the thermometer rising suddenly. As the exact composition of the product introduced into the flask is known, the weight of the residue will show how many molecules of the oxychloride have combined with one of the pentoxide, and it is found that equal numbers of molecules of the two substances have combined. All the excess of oxychloride above this proportion distils over, and the residue remaining in the flask, a straw-coloured, viscous mass, has therefore the empirical composition P_2O_5, $POCl_3$, or $(PO_2Cl)_n$. In its appearance and behaviour on distillation, this mass resembles the substance obtained by the action of chlorine on phosphorous oxide. If instead of distilling the product it is kept at 105—108°, and a slow stream of air passed over it, the same substance is obtained. As these results pointed to the formation of a compound polymeric with PO_2Cl, an attempt was now made to determine its molecular weight by some cryoscopic method. The choice of solvents is somewhat restricted.

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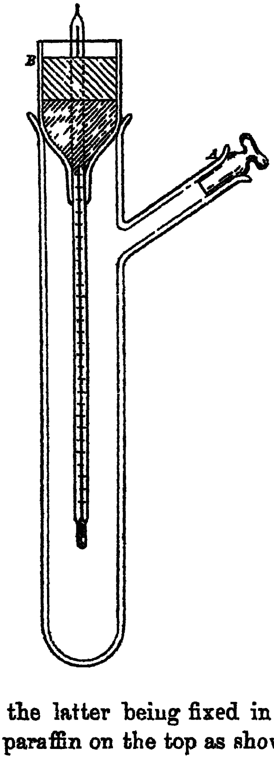
* In distilling this substance with a thermometer, or in passing a current of air over it, neither ordinary nor india-rubber corks can be used. A useful flask for distilling this or similar corrosive liquids is made by sealing on to the neck of an ordinary Wurtz flask about four inches of glass tubing of such a width that the thermometer or leading tube just slides in it. The thermometer is fixed in position by a small piece of india-rubber tubing.

Phosphoryl trichloride was finally chosen as the most convenient. It melts at about 0°; since there is already an excess of oxychloride present, the product is perfectly miscible: further, this excess does not interfere with the melting point, so that the depression produced is due only to the compound present. On the other hand, phosphoryl oxychloride is a difficult substance to keep in a pure state during the time required for a determination; it rapidly absorbs moisture from the air and from corks of any kind. The arrangement used is shown in Fig. 1. A glass tube B was drawn out at one end to nearly fit the thermometer, the latter being fixed in first with sulphur and then with a layer of paraffin on the top as shown by the shading, and the whole ground into the main tube. The thermometer was by Geissler, graduated to $\frac{1}{5}$° C., and reading by estimation to 0·01° C., a sufficiently good approximation for the purpose. As the molecular depression of phosphoryl trichloride has not hitherto been determined, preliminary experiments were made with phosphorus trichloride—a substance not known to have any chemical action on the oxychloride, and which can easily be obtained in a pure state.

FIG. 1.



A quantity of pure phosphoryl trichloride was prepared by heating phosphorus pentoxide with phosphorus pentachloride in sealed tubes at 120°. After a preliminary distillation, the resulting liquid still contains dissolved hydrogen chloride; the latter may be separated either by a current of dry air at 105°, or more conveniently by prolonged boiling with a reflux condenser in an apparatus composed wholly of glass. The pure substance is distilled directly into the freezing-point apparatus; its melting point, when freed in this way from dissolved gas, is +0·80°. The phosphorus trichloride was purified just before use in a similar manner. The results are tabulated below.

No. of experiment.	Weight of $POCl_3$ taken.	Weight of PCl_3 added.	Depression produced.	1/concentration.	$\frac{\text{Depression}}{\text{concentration}}$.
	grams	grams.	C.		
(I)	41·62	0·90	1·20°	46·2	55·5
(II)	41·62	3·30	4·20	12·6	53·0
(III)	44·21	1·37	1·62	32·3	52·3
(IV)	41·21	3·30	4·02	13·4	53·9

The last two observations were made on fresh preparations. The whole four lie on a straight line within the error of experiment, so that up to concentrations of 8 per cent. the depression of the freezing point is proportional to the concentration. Hence, 1 gram-molecule of phosphorus trichloride, dissolved in 100 gram-molecules of phosphoryl trichloride, produces a depression of the freezing point of 0·48°, a number differing considerably from the 0·63° of Raoult. From this we deduce the latent heat of fusion to be 20·3 cal., using van't Hoff's formula $\lambda = \frac{0·02T^2}{M\,.\,\delta\theta}$. So far as I am aware, this constant has not been directly determined.

The observations on the product were—

No. of experiment.	Weight of $POCl_3$.	Weight of stuff added.	Depression produced.	1/concentration.	$\frac{\text{Depression}}{\text{concentration}}$.
	grams	grams	C.		
(I)......	44·52	0·393	0·39°	113·3	44·2
(II)......	45·30	0·826	0·84	54·8	46·1

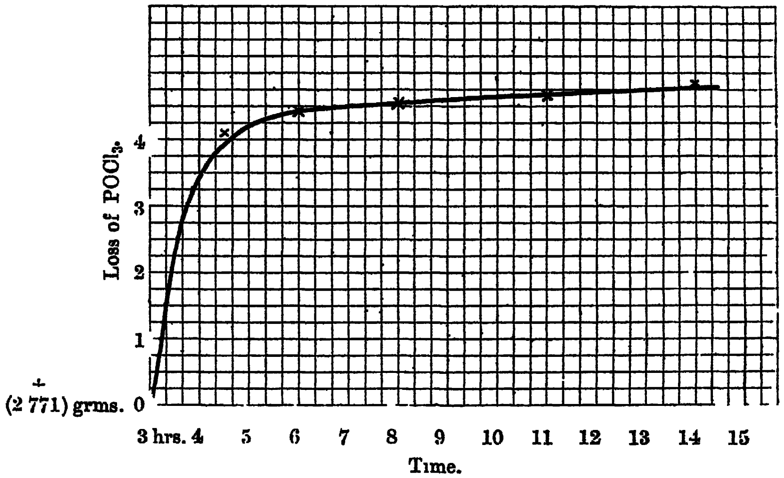
On the assumption that the oxychloride passing over on distillation is uncombined, this gives a molecular weight of 163. PO_2Cl requires

98·4; $P_2O_4Cl_2$, 196·8. But further investigation showed that the straw-coloured mass left on distillation is not a single substance, but contains at least two compounds. Hence, even if the further assumption be made that each of the substances present exerts its own osmotic pressure independently of the others, or, in other words, that Dalton's law of pressures holds for such a solution, the result is only the mean molecular weight of two or more compounds.

The residue obtained on distillation was now further examined. If it consists merely of a solution of phosphorus pentoxide in phosphoryl trichloride, then, on treating it with a neutral solvent, such as dry carbon bisulphide, the oxychloride will dissolve, leaving a residue free from chlorine, and the carbon bisulphide solution will contain phosphorus and chlorine in the ratio of 1 : 3·42. If it consist of a single compound, such as $(PO_2Cl)_n$, it will either be altogether insoluble, or will dissolve. If only slightly soluble, the ratio of phosphorus to chlorine must be the same in both residue and solution, 1 : 1·14. The viscous residue was treated with small quantities of dry carbon bisulphide, until nothing further was dissolved. The solution, on treatment with water, gives the whole of its phosphorus as orthophosphoric acid, and has the ratio of phosphorus to chlorine at 1 : 2·28, agreeing with $P_2O_3Cl_4$, the pyrophosphoryl chloride of Geuther and Michaelis. The residue in the flask, after the extraction of the pyrophosphoryl chloride, has the invariable ratio of phosphorus to chlorine of 1 : 0·79.

It has already been mentioned that the substance commences to dissociate at 150°. At low temperatures (105—108°), and in a very slow stream of air, that is, with a high partial pressure, the dissociation is practically *nil*. At the same temperature, in a rapid stream of air, equivalent to a reduction of the pressure, more phosphoryl chloride is lost. The same result is obtained with the higher pressure at 150°. The curve shows the loss of weight with time in a slow, steady stream of dry air at 150°; the curve is of the logarithmic form, usual in cases of dissociation.

If a bulb full of the solution containing excess of phosphoryl trichloride is added to pure dry carbon bisulphide, the liquid is turbid, but, on standing for some time in a well-closed flask, becomes clear, minute drops of liquid being deposited on the sides of the flask. The ratio of phosphorus to chlorine for the original substance being as 1 : 2·367, and for the clear carbon bisulphide solution as 1 : 3·18; it is evident from the previous discussion that, besides the excess of oxychloride, some other compound, containing less chlorine, has gone into solution. As before, the reaction of this solution with water agrees with the supposition that pyrophosphoryl chloride is present, since here again only orthophosphoric acid is formed. The insoluble



drops, precipitated on the sides of the flask, after being washed with fresh bisulphide, give, on analysis, practically the same ratio of phosphorus to chlorine as before, namely, as 1 : 0·82.

In another experiment, where the ratio of phosphorus to chlorine for the original substance was 1 : 2·67, the clear solution gave 1 : 3·01, and the well washed residue, which weighed 14·7 per cent. of the whole, as 1 : 0·79. A different preparation gave for the same ratio, original substance 1 : 2·14, clear solution as 1 : 2·65. Hence, on treating the contents of the tube directly with carbon bisulphide, some pyrophosphoryl chloride, together with the excess of phosphoryl trichloride, goes into solution, leaving a residue of constant composition, for which the ratio of phosphorus to chlorine is 1 : 0·81. From the value of the ratio found in the carbon bisulphide solution, the relative proportions of pyrophosphoryl and phosphoryl chlorides have been calculated. It differs in different preparations, and agrees with no simple reaction. It is quite evident from this that the reaction is a complicated one, and is not represented by the equation $P_2O_5 + POCl_3 = 3PO_2Cl$, given by Gustavson, and reproduced in some of the larger text-books.

Since the boiling points of pyrophosphoryl chloride and phosphoryl trichloride differ by over 100°, it was thought that further evidence might be obtained by fractional distillation in a vacuum. Some of the original product was, therefore, placed in a small Würtz flask with a long condensing tube, which was then rapidly exhausted by the Sprengel pump, and sealed. As each fraction came over, the end of the condenser containing the liquid was fused off, and the liquids analysed. At 100°, the distillate was pure phosphoryl trichloride, an analysis of this fraction giving 69·5 per cent. of chlorine instead of 69·34. At 180°, an equal number of molecules of pyrophosphoryl and phosphoryl chlorides came over; this requires the ratio of phosphorus to chlorine to be as 1 : 2·67; found 1 : 2·68.

The chemical reactions of the product obtained by the action of phosphoryl trichloride upon phosphorus pentoxide are not very definite. If it be assumed that all the oxychloride above the proportion $P_2O_5 : POCl_3$ is uncombined, and the distillation experiments lead to this conclusion, then the reaction with ice-cold water is $2n(PO_2Cl) + 3nH_2O = nHPO_3 + nH_3PO_4 + 2nHCl$; half the phosphorus appearing as metaphosphoric acid and the other half as orthophosphoric acid. With absolute alcohol containing just sufficient sodium ethylate to combine with all the chlorine, the chief product is diethylphosphoric acid, $PO(OH)(OC_2H_5)_2$, of which the barium salt and insoluble lead salt were prepared, and the identity of which was determined by analysis.

With glacial acetic acid, the product gives a dark brown solution. On distillation, the whole of the chlorine present passes over as acetyl chloride, leaving a tarry, viscous mass in the flask.

The results arrived at may be summarised as follows:—

(1.) There is not at present any evidence to show that a substance having the composition PO_2Cl, or any multiple of this, exists.

(2.) The reaction of phosphoryl trichloride on phosphorus pentoxide at 200° is not represented by the equation $P_2O_5 + POCl_3 = 3PO_2Cl$, but is much more complex than this.

(3.) That at least two compounds are formed in the reaction, one of which is pyrophosphoryl chloride, $P_2O_3Cl_4$, and the other, which may prove to be a mixture, is of constant composition, and from its analysis cannot have a simpler formula than $P_7O_{15}Cl_5$.

(4.) I have shown, incidentally, that the molecular depression of the freezing point for phosphoryl trichloride, 0·48°, differs considerably from the "normal" or average value given by Raoult, 0·63°.

In conclusion, my thanks are due to Professor Thorpe, to whom I am much indebted for advice and assistance throughout this work.

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XXIV.—*Chlorinated Phenylhydrazines.*

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In the following paper, orthochlorophenylhydrazine and some of its more important derivatives are described, and an account is also given of the action of carbamide on parachlorophenylhydrazine. The work was undertaken at the instance of Dr. Ruhemann, to whom I owe my best thanks for help afforded me during this investigation.

The *orthochlorophenylhydrazine hydrochloride*, $C_6H_4Cl{\cdot}NH{\cdot}NH_2,HCl$ [Cl : N = 1 : 2], was prepared from orthochloraniline; 45 grams of the latter were dissolved in 675 grams of concentrated hydrochloric acid, and diazotised by 26 grams of sodium nitrite dissolved in 180 grams of water. The solution of the orthochloraniline was well cooled in a freezing mixture, and the sodium nitrite solution added in small quantities at a time, the mixture being allowed to stand between each addition until the nitrous smell had disappeared. The solution was then rapidly filtered, and 152 grams of stannous chloride dissolved in an equal weight of concentrated hydrochloric acid added. Instead of an immediate, bulky, white precipitate, as is usually the case in the preparation of aromatic hydrazines, the hydrochloride did not come down for about half an hour, when the solution became pasty owing to the formation of long crystals of the hydrochloride, which were collected and dried on porous plates. As the hydrochloride thus prepared carries down with it a considerable amount of tin, its aqueous solution was treated with sulphuretted hydrogen, the tin sulphide filtered off, the filtrate decolorised with animal charcoal, when necessary, and evaporated on the water-bath.

After drying, the salt gave on analysis numbers agreeing with the formula $C_6H_4Cl{\cdot}NH{\cdot}NH_2,HCl$.

	Calculated for $C_6H_8N_2Cl_2$.	Found. I.	II.	III.
C	40·22	40·82	—	—
H	4·47	5·09	—	-
N	15·64	—	15·81	—
Cl	39·67	—	—	39·41

The hydrochloride forms long, colourless needles, which darken at 181—183°, and melt at 190° with decomposition. It is readily soluble in water and alcohol, and the aqueous solution reduces Fehling's solution and mercuric chloride.

The *hydrazine* was first obtained by the addition of potash to the aqueous solution of the hydrochloride and extraction with ether; on distilling off the ether, an oily liquid was left. Attempts were made to distil this, but even at a pressure of 45 mm. it was found that the oil split up on distillation, yielding orthochloraniline and ammonia. The base was then isolated by treating the hydrochloride with a concentrated solution of sodium acetate, agitating with ether, evaporating the ethereal solution, and drying the residue over calcium chloride for some days, when a clear, orange-coloured oil was obtained. A chlorine determination of this oil showed it to be orthochlorophenylhydrazine, $C_6H_4Cl{\cdot}NH{\cdot}NH_2$.

	Calculated for $C_6H_7ClN_2$.	Found.
Cl	24·91	24·49

Orthochlorophenylsemicarbazide is produced on adding a solution of potassium cyanate to orthochlorophenylhydrazine dissolved in water. If the solutions are concentrated, the mixture nearly solidifies to a mass of colourless plates, which are recrystallised from boiling water, in which they are sparingly soluble. This compound melts at 164°, and gave on analysis numbers corresponding with the formula $C_6H_4Cl{\cdot}NH{\cdot}NH{\cdot}CONH_2$.

	Calculated for	Found.		
	$C_7H_8N_3ClO$.	I.	II.	III.
C	45·29	44·73	45·68	—
H	4·31	5·53	4·01	—
N	19·14	—	—	19·70

Orthochlorophenyl-phenylthiosemicarbazide is formed on adding phenylthiocarbimide to an ethereal solution of the free hydrazine On evaporating the ether, thin, yellow plates are left, which when recrystallised from alcohol melt at 134°. The following values correspond with the formula $C_6H_4Cl{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$.

	Calculated for $C_{13}H_{12}ClN_3S$.	Found.
Cl	12·79	12·97
S	11·53	11·23

An ethereal solution of this compound acquires a deep green colour when shaken with an aqueous solution of copper sulphate; this is intensified on addition of ammonia.

Orthochlorophenylhydrazinepyruvic Acid,

$$C_6H_4Cl{\cdot}NH{\cdot}N{:}C(CH_3){\cdot}COOH.$$

—On adding pyruvic acid to the free hydrazine or, better, to an aqueous solution of the hydrochloride, a lemon-yellow flocculent precipitate is thrown down consisting of needles which, after recrystallisation from alcohol, melt at 178°. This substance gave on analysis the following numbers:—

	Calculated for $C_9H_9N_2ClO_2$.	Found. I.	II	III.
C	50·82	50·65	—	—
H	4·23	4·58	—	—
N	13·18	—	13·28	—
Cl	16·71	—	—	16·38

This acid is readily soluble in alcohol, alkalis, and ammonia, but insoluble in sodium carbonate.

The *ethyl salt* is readily obtained by heating the alcoholic solution of the acid for some time with the addition of a few drops of sulphuric acid. On adding water to the solution, a nearly colourless aggregate of needles is thrown down, which after recrystallisation from dilute alcohol melt at 168°.

Aldehydes and ketones (such as benzaldehyde, acetone, and acetophenone), added to solutions of the hydrochloride, yield colourless or pale-yellow precipitates on the addition of a concentrated solution of sodium acetate, but the compounds thus formed are so unstable that I was unable to further investigate them.

Parachlorophenylhydrazine has already been described by Elsingshorst (*Inaug. Dissert.*, *München*, 1884); I have studied its reactions with certain substances closely related to urea. Fischer has studied the reaction of phenylhydrazine with potassium isocyanate (*Annalen*, **190**, 113), whilst Pellizari (*Gazzetta*, **16**, 200) and Pinner (*Ber.*, **20**, 2358) both acted on this hydrazine with carbamide. In both cases phenylsemicarbazide resulted. This work on the reactions of carbamide derivatives with phenylhydrazine was further extended by Skinner and Ruhemann (Trans., **53**, 550), who heated ethyl carbamate with phenylhydrazine, obtaining diphenylcarbazide; they also completed the series of semicarbazides and carbazides containing phenyl groups, by acting on phenylhydrazine with other compounds related to carbamide.

Action of Parachlorophenylhydrazine on Ethyl Carbamate.—A mixture of 2 mols. of parachlorophenylhydrazine with 1 mol. of ethyl carbamate was heated over a small flame until ammonia ceased to be evolved. On cooling, the liquid solidified to a mass of crystals, which on washing with ether were obtained colourless. They are somewhat soluble in boiling water, readily in hot alcohol, melt at a temperature above 250°, and give no colour reactions with copper sulphate, mercuric chloride, or ammonia. Analysis showed that they were not the carbazide but diparachlorophenylcarbamide,

$CO<\begin{matrix}NH\cdot C_6H_4Cl\\NH\cdot C_6H_4Cl\end{matrix}$.

	Calculated for $C_{13}H_{10}N_2Cl_2O$.	Found. I.	Found. II.
Cl	26·19	—	26 58
N	10·33	10·52	—

The ether used for washing the crystals of the disubstituted carbamide left a crop of colourless crystals on evaporation, which I intend to examine further.

Parachlorophenyl-phenylsemithiocarbazide.—The semithiocarbazide, $C_6H_4Cl\cdot NH\cdot NH\cdot CS\cdot NH\cdot C_6H_5$ [Cl : N = 1 : 4], was obtained by adding phenylthiocarbimide to an ethereal solution of the hydrazine. On evaporation, yellow crystals were deposited which are sparingly soluble in hot alcohol, and crystallise from it in pale-yellow plates melting at 149°. They gave the following numbers on analysis :—

	Calculated for $C_{13}H_{12}N_3SCl$.	Found.
Cl	12·79	12·98
S	11·53	11·85

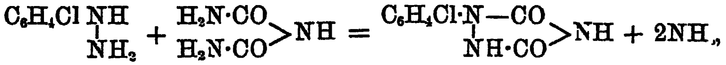
An ethereal solution of this compound becomes green when shaken with an aqueous solution of copper sulphate, and this colour is not destroyed on the addition of ammonia. The colour reaction is analogous to that pointed out by Skinner and Ruhemann (*loc. cit.*) for phenylsemithiocarbazide.

Parachlorophenylurazole.—Pinner was the first to prepare phenylurazole by heating one part of phenylhydrazine hydrochloride with one and a half parts of carbamide (*Ber.*, **20**, 2358). The same compound was afterwards prepared by Skinner and Ruhemann (*loc. cit.*) by heating phenylhydrazine with biuret. The latter method was employed to convert parachlorophenylhydrazine into parachlorophenylurazole. Equal weights of biuret and parachlorophenylhydrazine were heated over a small flame, ammonia was evolved, and on cooling the mass solidified. This was extracted with hot dilute alcohol, boiled with animal charcoal, filtered, and crystallised, when aggregates of needles melting at 266° were deposited. A chlorine estimation showed this substance to be parachlorophenylurazole,

$\begin{matrix}C_6H_4Cl\cdot N—CO\\ \mid \qquad\\ NH\cdot CO\end{matrix}>NH$ [Cl : N = 1 : 4].

	Theory for $C_8H_6N_3ClO_2$.	Found.
Cl	16·31	16·37

The reaction takes place according to the equation



$$C_6H_4Cl\begin{matrix}NH\\|\\NH_2\end{matrix} + \begin{matrix}H_2N{\cdot}CO\\H_2N{\cdot}CO\end{matrix}{>}NH = \begin{matrix}C_6H_4Cl{\cdot}N-CO\\|\qquad\\NH{\cdot}CO\end{matrix}{>}NH + 2NH_3,$$

being analogous to that observed in the formation of phenylurazole

Parachlorophenylhydrazine Parabanate.—A parabanate of phenylhydrazine was prepared by Skinner and Ruhemann by the addition of a concentrated solution of sodium acetate to a mixture of solutions of phenylhydrazine hydrochloride and parabanic acid. The corresponding parabanate of parachlorophenylhydrazine may be obtained in a similar manner. Parachlorophenylhydrazine hydrochloride dissolved in water is added to a solution of parabanic acid, and treated with an excess of sodium acetate solution. After the lapse of a few minutes, groups of needles separate, which melt at 213° with decomposition. A chlorine determination showed that this parabanate contains 1 mol H_2O, like the phenylhydrazine parabanate. The formula $C_3O_3N_2H_2,2(C_6H_7N_2Cl),H_2O$ requires:—

	Theory for $C_{15}H_{18}N_6O_4Cl_2$.	Found.
Cl	17·02	17·00

The parabanate is slighty soluble in boiling water, probably owing to the formation of an oxalurhydrazide,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_4Cl.$$

Action of Chloroform and Alcoholic Potash on Parachlorophenylhydrazine.—The isonitrile reaction was applied to parachlorophenylhydrazine with the view of preparing the parachlorinated derivative of diphenyltetrazine. A mixture of chloroform with an alcoholic solution of parachlorophenylhydrazine was treated with alcoholic potash. The reaction started by itself, and was completed by heating for some time on the water-bath. The product of the reaction was then allowed to cool, and after addition of water shaken with ether; the ethereal solution was then agitated with dilute sulphuric acid in order to remove the unaltered hydrazine. On evaporating the ether, a dark-coloured residue was left, which was boiled with water and filtered from a resinous matter; the hot filtrate deposited colourless needles on concentration. These darken at 135° and melt at 152°. A nitrogen determination showed this compound to be formyl-parachlorophenylhydrazine, $C_6H_4Cl{\cdot}NH{\cdot}NH{\cdot}CHO$.

	Calculated for $C_7H_7N_2ClO$.	Found.
N	17·67	17·43

The resinous mass left on the filter yielded minute crystals on allowing it to stand for about a week; these probably consisted of the desired tetrazine, but the amount obtained was not sufficient for analysis. I hope shortly to return to the study of this reaction, and to communicate to the Society the results arrived at in the case of this and other chlorinated phenylhydrazines.

University Laboratory,
Cambridge.

XXV.—*Action of Reducing Agents on αα'-Diacetylpentane. Synthesis of Dimethyldihydroxyheptamethylene.*

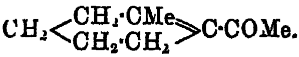
By F. STANLEY KIPPING, Ph.D., D.Sc., and W. H. PERKIN, Junr., Ph.D., F.R.S.

αα'-Diacetylpentane, a diketone which has the constitution

$$COMe\cdot[CH_2]_5\cdot COMe,$$

as is proved by its method of preparation and properties (compare Trans., 1889, 55, 330), behaves in a most remarkable manner both with dehydrating and with reducing agents.

When treated with concentrated sulphuric acid under suitable conditions, it is converted into a compound of the composition $C_9H_{14}O$, which, as has been previously shown (Trans., 1890, 57, 13), is, doubtless, a methylacetyltetrahydrobenzene of the constitution

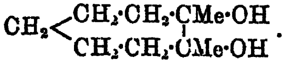


$$CH_2<\begin{matrix}CH_2\cdot CMe\\CH_2\cdot CH_2\end{matrix}>C\cdot COMe.$$

On reduction with sodium in moist ethereal solution, αα'-diacetylpentane yields as principal product a colourless liquid of the composition $C_9H_{18}O_2$; the formation of this compound is represented by the equation

$$C_9H_{16}O_2 + H_2 = C_9H_{18}O_2.$$

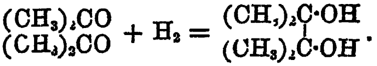
The method of preparation, properties, and some derivatives of this reduction product are described in the present paper, as are also various experiments which were made with the object of ascertaining its constitution; the results of these experiments seem to prove satisfactorily that the compound in question is a dimethyldihydroxyheptamethylene of the constitution



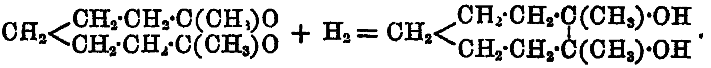
$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CMe\cdot OH\\CH_2\cdot CH_2\cdot CMe\cdot OH\end{matrix}.$$

The formation of a heptamethylene derivative in this simple manner is an extremely interesting reaction, which may be regarded as analogous to the production of pinacone from acetone; the only difference between the two reactions is that in the formation of pinacone, combination takes place between two carbon atoms of two different acetone molecules, yielding an open-chain compound, whereas in the case of dimethyldihydroxyheptamethylene a closed-chain derivative is formed by the union of two carbon atoms of one and the same molecule of diacetylpentane.

The analogy between the two reactions is clearly shown with the aid of the following equations :—



$$\begin{matrix}(CH_3)_2CO\\(CH_3)_2CO\end{matrix} + H_2 = \begin{matrix}(CH_3)_2C{\cdot}OH\\ |\\(CH_3)_2C{\cdot}OH\end{matrix}.$$



$$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2{\cdot}C(CH_3)O\\CH_2{\cdot}CH_2{\cdot}C(CH_3)O\end{matrix} + H_2 = CH_2{<}\begin{matrix}CH_2{\cdot}CH_2{\cdot}C(CH_3){\cdot}OH\\ |\\CH_2{\cdot}CH_2{\cdot}C(CH_3){\cdot}OH\end{matrix}.$$

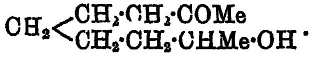
Constitution of the Reduction Product of αα′-Diacetylpentane.

In endeavouring to assign the correct constitutional formula to the reduction product of diacetylpentane, it is, in the first place, important to notice that the compound in question is formed by the addition of only two atoms of hydrogen to the diketone, a fact which is conclusively proved by the results of twelve analyses. Although many different samples have been analysed, the quantity of hydrogen found was never more than 11·75 per cent., usually about 11·5 per cent., results which agree very closely with those required for a compound of the composition $C_9H_{18}O_2$, which contains 11·39 per cent. of hydrogen.

A compound of the constitution $OH{\cdot}CHMe{\cdot}[CH_2]_5{\cdot}CHMe{\cdot}OH$ which, it might be expected, would be produced by the reduction of the diketone, is evidently not formed in any appreciable quantity under the conditions employed in our experiments, as such a compound would contain 12·5 per cent. of hydrogen.

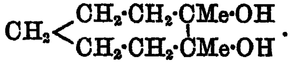
Now a compound of the composition $C_9H_{18}O_2$, obtained by reducing αα′-diacetylpentane, $COMe{\cdot}[CH_2]_5{\cdot}COMe$, may, theoretically, have the constitution represented by one of the following formulæ :—

I.



$$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2{\cdot}COMe\\CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH\end{matrix}.$$

II.



$$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2{\cdot}CMe{\cdot}OH\\ |\\CH_2{\cdot}CH_2{\cdot}CMe{\cdot}OH\end{matrix}.$$

If its constitution be expressed by formula I, it would, in all probability, show the following behaviour :—

1. It would combine with hydroxylamine to form an oxime of the constitution $OH{\cdot}N{:}CMe{\cdot}[CH_2]_5{\cdot}CHMe{\cdot}OH$, and with phenylhydrazine to form a hydrazone of the composition $C_9H_{18}O{:}N_2HPh$.

2. It would be converted into a monacetyl-derivative of the constitution $COMe{\cdot}[CH_2]_5{\cdot}CHMe{\cdot}OAc$, on treatment with acetic anhydride.

3. When treated with hydrobromic acid, a monobromo-derivative of the constitution $COMe{\cdot}[CH_2]_5{\cdot}CHMeBr$ would be produced, whereas phosphorus pentabromide would convert it into a tribromide of the constitution $CMeBr_2{\cdot}[CH_2]_5{\cdot}CHMeBr$.

4. It would be easily reduced to a dihydric alcohol of the constitution $OH{\cdot}CHMe{\cdot}[CH_2]_5{\cdot}CHMe{\cdot}OH$ by sodium amalgam, zinc-dust and hydrochloric acid, or some other suitable reducing agent.

5. When heated with concentrated hydriodic acid and amorphous phosphorus at a high temperature, it would be converted into a hydrocarbon of the paraffin series having the constitution

$$CH_3{\cdot}[CH_2]_7{\cdot}CH_3.$$

The behaviour of the reduction product with each of the reagents just enumerated was carefully examined, in most cases the experiments being repeated several times under varied conditions; the results were, however, completely at variance with those which, in all probability, would have been obtained had the reduction product been a ketone alcohol; its constitution cannot, therefore, be represented by formula I.

On the other hand, the chemical behaviour of the reduction product is exactly what might be expected, assuming that it is a dihydroxy-compound of the constitution expressed by formula II; this will be evident from a consideration of the following facts:—

1. It does not combine with hydroxylamine or with phenylhydrazine.

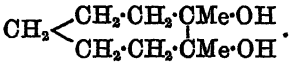
2 It yields a diacetyl-derivative of the composition $C_{13}H_{22}O_4$ with acetic anhydride.

3. Phosphorus pentabromide converts it into a dibromide of the composition $C_9H_{16}Br_2$; this substance seems also to be formed with difficulty on prolonged heating with concentrated hydrobromic acid.

4. It is not acted on by such reducing agents as zinc and hydrochloric acid in alcoholic solution, sodium amalgam, sodium and alcohol.

5. On reduction with hydriodic acid and amorphous phosphorus, it is converted into a hydrocarbon of the composition C_9H_{18}.

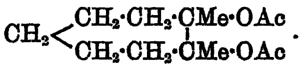
These facts are, we believe, amply sufficient to warrant the conclusion that the reduction product of *αα'*-diacetylpentane is a dimethyldihydroxyheptamethylene of the constitution



$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CMe\cdot OH\\ CH_2\cdot CH_2\cdot CMe\cdot OH\end{matrix}.$$

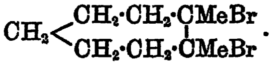
The derivatives of this compound, which are referred to above, and described in the experimental part of the paper, have, therefore, the constitutions represented by the following formulæ:—

Dimethyldihydroxyheptamethylene diacetate,



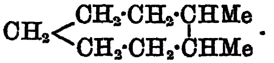
$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CMe\cdot OAc\\ CH_2\cdot CH_2\cdot CMe\cdot OAc\end{matrix}.$$

Dimethyldibromoheptamethylene,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CMeBr\\ CH_2\cdot CH_2\cdot CMeBr\end{matrix}.$$

Dimethylheptamethylene,



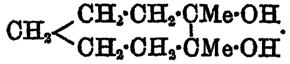
$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CHMe\\ CH_2\cdot CH_2\cdot CHMe\end{matrix}.$$

The compounds obtained in the course of this investigation are, we believe, the first and only derivatives of the 7-carbon ring—heptamethylene—which have yet been prepared, and the constitution of which has been proved with any degree of certainty.

Markownikoff has, however, lately published an interesting paper on some compounds obtained from suberone (*Compt. rend.*, **110**, 466—468), which, including suberone itself, he considers to be derivatives of heptamethylene; and by reducing suberonyl alcohol with hydriodic acid, he obtained a hydrocarbon of the composition C_7H_{14}, which he supposes to be heptamethylene.

It appears to us that the results obtained by Markownikoff can be equally well explained on the assumption that suberone is a methylketohexamethylene, a dimethylketopentamethylene, or some other ketopolymethylene derivative, and that as yet no evidence has been brought forward to warrant the conclusion that suberone is a heptamethylene derivative.

Dimethyldihydroxyheptamethylene



$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CMe\cdot OH\\ CH_2\cdot CH_2\cdot CMe\cdot OH\end{matrix}.$$

Dimethyldihydroxyheptamethylene (dimethylheptamethylene glycol) and small quantities of a condensation product of high molecular weight are obtained by the reduction of $\alpha\alpha'$-diacetylpentane in the following manner:—A solution of the pure diketone in 5 to 6 times its volume of pure ether is poured into a large bottle which contains about 150 c.c. of concentrated soda, and is provided with a reflux condenser. Sodium is then added in small portions at a time, any considerable rise of temperature being avoided by immersing the bottle in cold water. When the reduction has proceeded for some time, the metal becomes covered with a thick layer of a colourless sodium derivative of the glycol, and in some cases a considerable quantity of this compound is deposited on the sides of the vessel, but on agitating the alkaline liquid, it gradually passes into solution. The addition of sodium is continued until 6 to 8 times the quantity theoretically necessary for complete reduction, that is, 4 atoms of sodium to 1 mol. of the diketone, has been employed.

The ethereal solution is then separated, the alkaline liquid extracted once or twice with ether, the combined ethereal solutions very carefully dried over anhydrous potassium carbonate, filtered, and evaporated, when there remains a yellowish oil, the weight of which is about the same as that of the diketone employed. The crude product is submitted to fractional distillation under reduced pressure, say, 180 mm.; the thermometer quickly rises to 195°; almost the whole of the product passing over between 195° and 205°, the temperature then rises rapidly to about 300°, when a thick, yellowish oil collects in the receiver. The quantity of this compound of high boiling point is only about 3—6 per cent. of the crude reduction product; it will be referred to again hereafter.

The portion passing over between 195° and 205° consists of slightly impure dimethyldihydroxyheptamethylene, from which the pure compound can be easily obtained by submitting it to repeated fractional distillation under reduced pressure.

Analyses of various preparations of the pure compound gave the following results:—

I. 0·2016 gram substance gave 0·5062 gram CO_2 and 0·2098 gram H_2O.

II. 0·1852 gram substance gave 0·4624 gram CO_2 and 0·1923 gram H_2O.

III. 0·2112 gram substance gave 0·5266 gram CO_2 and 0·2178 gram H_2O.

	Calculated for $C_9H_{18}O_2$.	Found. I.	II.	III.
C	68·36 p. c.	68·5	68·1	68·0 p. c.
H	11·39 „	11·6	11·5	11·5 „
O	20·25 „	20·9	20·4	20·5 „

Dimethyldihydroxyheptamethylene is a moderately thick, colourless oil, with a sharp, burning taste, and a characteristic smell recalling that of thyme; it is specifically lighter than water, and is volatile with steam and alcohol vapour. It boils at 201° under a pressure of 180 mm., at 203—205° under a pressure of 186 mm., and at 180—185° under a pressure of 100 mm., the thermometer being entirely in the vapour in all three cases; when cooled below 0°, it becomes very thick, but shows no signs of crystallising even when kept below 0° for some time.

It is miscible with alcohol, ether, chloroform, glacial acetic acid, &c., in all proportions, but is only sparingly soluble in cold water, from which it separates again on warming or on adding sodium carbonate; it is insoluble in soda. It dissolves in concentrated sulphuric acid with development of heat, and it is also soluble in concentrated hydrobromic acid, although it quickly separates from the solution again, having been partially converted into an insoluble bromide. It does not combine with sodium hydrogen sulphite, hydroxylamine, or phenylhydrazine, but it is readily acted on by boiling acetic anhydride, yielding a diacetyl-derivative, and by phosphorus pentabromide, which converts it into an oily dibromide.

It is a curious fact that a mixture composed of about 94 per cent. of dimethyldihydroxyheptamethylene, and about 6 per cent. of water, has approximately the same boiling point as the anhydrous glycol, and is not separated into its constituents on fractional distillation under reduced pressure. This fact was brought under our notice at an early stage of the investigation in the following manner:—The ethereal solution of the crude reduction product of diacetylpentane, having been treated for a short time with anhydrous calcium chloride, was evaporated, the residue submitted to fractional distillation under a pressure of 150 mm., and the portion passing over between 197—199° collected separately.

Two analyses of this liquid gave the following results:—

I. 0·1760 gram substance gave 0·4161 gram CO_2 and 0·1854 gram H_2O.

II. 0·1432 gram substance gave 0·3386 gram CO_2 and 0·1528 gram H_2O.

	Calculated for $C_9H_{18}O_2$ + 6 p. c. H_2O.	Found I.	Found II.
C........	64·3 per cent.	64·5	64·5 per cent.
H........	11·4 „	11·7	11·7 „
O..	24·3 „	23·8	23·8 „

This fraction (b. p. 197—199°; 150 mm.) was distilled again under a pressure of 100 mm., the portion passing over between 182° and 186° collected separately, and analysed:—

0·1640 gram substance gave 0·3850 gram CO_2 and 0·1737 gram H_2O.

	Calculated for $C_9H_{18}O_2$ + 6 p. c. of H_2O.	Found.
C	64·3 per cent.	64·6 per cent.
H	11·4 ,,	11·7 ,,
O...........	24·3 ,,	23·7 ,,

Water is, doubtless, the impurity to which the low percentage of carbon found is due, because when anhydrous potassium carbonate is employed for drying the ethereal solution, other conditions remaining the same, the glycol is easily obtained in a pure condition; the experiments show, moreover, that the water cannot be eliminated by fractional distillation, just as is the case with other mixtures of like nature.

Sodium Derivative of Dimethyldihydroxyheptamethylene.

This compound frequently separates from the ethereal solution in the preparation of dimethyldihydroxyheptamethylene in the manner described above. In order to determine its composition, some of the substance adhering to the sides of the bottle, and out of contact with the aqueous alkali, was picked out, quickly washed with ether on a porous plate, and then kept for some days in a desiccator.

The analyses of three different samples obtained in this way, and quickly weighed from stoppered bottles, gave the following results:—

I. 0·3362 gram substance gave 0·1156 gram Na_2SO_4.
II. 0·2932 ,, ,, 0·1022 ,,
III. 0·3254 ,, ,, 0·1112 ,,

	Calculated for $C_9H_{17}O_2Na + H_2O$.	Found I	Found II.	Found III.
Na........	11·5 per cent.	11·1	11·3	11·1 per cent.

These analyses show that the compound is a mono-sodium derivative of the glycol, containing, very probably, 1 mol. of water. In spite of the hygroscopic nature of the substance, there is no reason to suppose that this view of its composition is incorrect, since ethyl sodaceto-acetate and other compounds of like nature have been proved to contain water of crystallisation.

The sodium derivative of the glycol is a colourless, semi-crystalline, deliquescent compound which gradually decomposes on exposure to the air or when heated at about 50—60° in the air; it melts below 100°, and is quickly decomposed by cold water, but rather slowly by very concentrated soda.

It is, perhaps, unnecessary to remark that the formation of a mono- instead of a di-sodium derivative, under the conditions described above, cannot be regarded as evidence against the view that the reduction product is a dihydroxyheptamethylene derivative.

Constitution of Dimethyldihydroxyheptamethylene.

In accordance with the views put forward in the introduction, the reduction product of diacetylpentane may, theoretically, have the constitution represented by one of two formulæ (p. 215); in one case it would be an open-chain ketone-alcohol, in the other a closed-chain dihydric alcohol. It was necessary, therefore, in the first place, to investigate its behaviour with phenylhydrazine and with hydroxylamine; the following experiments were made for this purpose.

Behaviour of the Reduction Product with Phenylhydrazine.—A small quantity (3 grams) of the crude reduction product was heated at about 100° for three hours in sealed tubes with phenylhydrazine hydrochloride (4·8 grams) and sodium acetate (4·5 grams) in dilute alcoholic solution. The clear solution was then diluted with a large volume of water, the precipitated oil extracted with ether, the ethereal extract washed with very dilute hydrochloric acid, dried over calcium chloride, and evaporated. The yellowish, oily product weighed 2·8 grams, and showed all the properties of the original reduction product; a qualitative examination showed that it contained a trace of nitrogen, but the quantity was so small that it was quite evident that the formation of a hydrazone had not taken place.

Behaviour of the Reduction Product with Hydroxylamine.—Two experiments were made under different conditions, in order to try and prepare an oxime of the reduction product of diacetylpentane, but both were unsuccessful. In the first, the crude reduction product (4 grams) was treated with hydroxylamine hydrochloride (4 grams) and potassium carbonate (3 grams) in dilute alcoholic solution for three days at the ordinary temperature. After evaporating most of the alcohol on the water-bath, the residue was extracted with ether, the solution dried over calcium chloride, and evaporated, when there remained a light-yellow oil (3·8 grams); this oil contained a trace of nitrogen, but was insoluble in alkalis, and possessed all the properties of the original reduction product.

In the second experiment, the pure compound (3 grams) was treated with hydroxylamine hydrochloride (1·4 grams) and potash (5 grams) in dilute methyl alcoholic solution according to Auwers' method. After keeping the mixture for two days at the ordinary temperature, the alcohol was evaporated, the oil extracted with ether, the ethereal solution washed with very dilute hydrochloric acid, dried over calcium chloride, and evaporated. There remained a yellowish oil (2·4 grams) which did not contain a trace of nitrogen, and which showed all the properties of the original compound.

Behaviour of the Reduction Product with Reducing Agents.—Although the above experiments had shown pretty conclusively that the reduction product does not contain a carbonyl group, it seemed advisable to obtain further experimental proof that such is in reality the case by investigating its behaviour with reducing agents in the manner described below:—

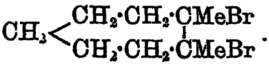
Exp. 1.—The pure reduction product (about 20 grams) was dissolved in alcohol, and zinc-dust and hydrochloric acid added to the boiling solution in small portions at a time, the operation taking about three hours; the solution was then diluted with water, the precipitated oil extracted with ether, and again submitted to the same treatment with zinc-dust and hydrochloric acid. Finally, the product was fractionated, and the portion passing over between 205° and 215° (210 mm.), which formed about 70 per cent. of the whole, collected separately and analysed; the percentage of hydrogen was found to be 11·6, proving that in this case also reduction had not taken place.

Exp. 2.—The original reduction product was dissolved in dilute alcohol, and a large quantity of sodium amalgam added to the boiling solution, in small portions at a time. The product, isolated in the usual manner, was fractionated under a pressure of about 280 mm., and the portion boiling at 200—210° collected for analysis. It was found to contain 11·57 per cent. of hydrogen, and to possess all the properties of the original compound.

Exp. 3.—The pure compound (16 grams) was dissolved in alcohol (100 grams), and sodium added in small portions at a time, the process being continued until a large excess (26 grams) of the metal had been employed, dilute alcohol being added from time to time whenever the reaction began to slacken. The alcohol was then evaporated as completely as possible, the residue diluted with water, the precipitated oil extracted with ether, dried, and fractionated under reduced pressure. Two analyses, made with different portions of the product, gave 11·72 and 11·76 per cent. of hydrogen respectively, proving conclusively that reduction had not taken place, since the addition of 2 atoms of hydrogen to the original reduction product would increase the percentage of hydrogen from 11·4 to 12·5 per cent.

Up to this stage of the investigation, it had been proved that the reduction product of diacetylpentane cannot be a ketone-alcohol of the constitution represented by formula I (p. 215); the following experiments show that it is a dihydric alcohol of the composition $C_9H_{18}O_2$.

Dimethyldibromoheptamethylene,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CMeBr\\ \vert\\ CH_2\cdot CH_2\cdot CMeBr\end{matrix}.$$

When the reduction product is treated with phosphorus pentabromide under suitable conditions, it is converted into a dibromide of the composition $C_9H_{16}Br_2$, which has, doubtless, the constitution assigned to it above. Before describing the preparation and properties of this dibromide, it will be as well, perhaps, to give a short account of the behaviour of the reduction product with hydrobromic acid.

A considerable quantity of the pure compound was heated at 100—115° in sealed tubes for about two hours with five times its volume of concentrated hydrobromic acid; on opening the tubes, it was found that the contents had separated into two layers, the upper one consisting of a dark-coloured oil. This oil was extracted from the diluted and partially neutralised solution by means of ether, the ethereal extract washed, dried, and evaporated, and the residue distilled under reduced pressure (about 140 mm.). The whole passed over between 160° and 220°, but no constant boiling point could be observed; the portion boiling at 160—200° was collected and analysed, and found to contain only 39 per cent. of bromine. As a compound of the composition $C_9H_{17}BrO$ contains 36·1, and a compound of the composition $C_9H_{16}Br_2$ 56·3 per cent. of bromine, it would seem that the liquid analysed consisted principally of the monobromide. In order to try and convert it into the dibromide, the whole of the distilled product was again heated at about 120° for several hours with a large excess of concentrated hydrobromic acid. The dark reddish-brown, heavy oil, obtained in this way, was distilled under a pressure of about 70 mm., and the portion boiling at 160—167° collected separately; the analysis of this fraction gave the following result:—

0·1758 gram substance gave 0·2047 gram AgBr.

	Calculated for		
	$C_9H_{17}BrO$.	$C_9H_{16}Br_2$.	Found.
Br..........	36·1 p. c.	56·3 p. c.	49·5 p. c.

These experiments show that the reduction product is partially converted into a dibromide by concentrated hydrobromic acid, a fact which is of considerable importance as a proof that it is a dihydric alcohol; as, however, the change is only incomplete even after prolonged heating with the acid, a more suitable method had to be employed for the preparation of the dibromide.

For this purpose, a small quantity of the pure reduction product is dissolved in a large volume of anhydrous chloroform, and a fair excess of the theoretical quantity of phosphorus pentabromide gradually added; evolution of hydrogen bromide quickly commences, and, after keeping for some time at the ordinary temperature, the reaction is at an end. The solution is decanted from the unchanged pentabromide, poured into cold water, and as soon as the decomposition of the phosphorus oxybromide is complete, the chloroform solution of the dibromide is separated, washed with dilute sodium carbonate and water consecutively, dried over calcium chloride, and the chloroform evaporated on the water-bath, when dimethyldibromoheptamethylene remains as a thick yellowish oil.

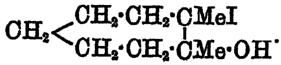
A bromine determination, made with a portion of the product which had been kept for 24 hours over sulphuric acid and paraffin, gave the following result:—

0·1036 gram substance gave 0·1370 gram AgBr.

	Calculated for $C_9H_{16}Br_2$.	Found.
Br	56·3 per cent.	54·8 per cent.

Dimethyldibromoheptamethylene is a thick, almost colourless oil with a sweetish, rather unpleasant smell; it is specifically heavier than, and insoluble in, water, but miscible with most ordinary organic solvents in all proportions. It seems to undergo slight decomposition when it is kept over sulphuric acid under reduced pressure.

Dimethylhydroxyiodoheptamethylene,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CMeI\\ CH_2\cdot CH_2\cdot CMe\cdot OH\end{matrix}.$$

When the glycol obtained from diacetylpentane is heated with hydriodic acid of sp. gr. 1·96, it seems to be almost completely converted into the moniodide, $C_9H_{17}OI$; the diiodide, $C_9H_{16}I_2$, if produced at all, is only formed in very small quantities.

The moniodide was prepared in the following manner:—The pure glycol was mixed with a considerable quantity of hydriodic acid of sp. gr. 1·96, and the mixture heated on the water-bath in a flask provided with a reflux condenser, first at a moderately low temperature, and then for about two hours at 100°. A portion of the contents of the flask was then distilled off, because it was thought that the diiodide would probably be more volatile than the moniodide, and if any of the former had been produced, it would collect in the receiver, leaving the moniodide behind. The small quantity of oil in the acid distillate was extracted with ether, the solution washed with dilute sodium carbonate and water, consecutively, dried over calcium chloride, and evaporated. The colourless oil obtained in this way was kept over sulphuric acid under reduced pressure for about 12 hours, and then an iodine determination carried out with the following result:—

0·1735 gram substance gave 0·1622 gram AgI.

	Calculated for $C_9H_{17}IO$.	Found.
I	47·29 per cent.	50·49 per cent.

The compound obtained by distillation as described above evidently consists principally of the moniodide, but contains a little of the diiodide; the former can be isolated in a pure condition from the residue in the flask by extracting with ether, and evaporating the washed and dried solution.

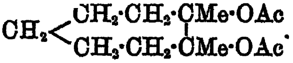
A portion of the oil (which remained in the flask) was kept under reduced pressure, and analysed with the following result:—

0·1661 gram substance gave 0 1455 gram AgI.

	Calculated for $C_9H_{17}IO$.	Found.
I	47·29 per cent.	47·06 per cent.

Dimethylhydroxyiodoheptamethylene is a colourless, mobile oil with a pleasant sweetish smell; it is readily soluble in ether, alcohol, and most ordinary organic solvents, but insoluble in water. It gradually decomposes, and turns brown on keeping, but it seems to boil without decomposition when heated in small quantities under the ordinary pressure.

Dimethylheptamethylene Diacetate,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CMe\cdot OAc\\ |\\ CH_3\cdot CH_2\cdot CMe\cdot OAc\end{matrix}.$$

When the reduction product of diacetylpentane is treated with acetic anhydride under suitable conditions, it is completely converted into a diacetyl derivative of the composition $C_9H_{16}(OAc)_2$; the formation of this diacetyl derivative is one of the strongest proofs that the compound described above as dimethyldihydroxyheptamethylene contains two hydroxy-groups.

In preparing the diacetyl derivative, the pure glycol is dissolved in excess of acetic anhydride, and the mixture boiled for about 2½ hours in a flask provided with a reflux condenser; the acetic anhydride is then partially distilled off under the ordinary pressure, and the residue submitted to fractional distillation under a pressure of 65 mm. The thermometer rises rapidly to about 180°, a small quantity only passing over below 190°; the thermometer then remains fairly constant, and between 192° and 207° about 70 per cent. of the whole passes over, the thermometer finally rising to about 215°.

The fraction boiling at 192—207° was fractionated again under the same pressure, and the portion boiling constantly at 199—202° collected separately.

The analysis of this fraction gave results which agreed well with those required by a diacetyl derivative of dimethyldihydroxyheptamethylene.

0·1555 gram substance gave 0·3681 gram CO_2 and 0·1323 gram H_2O.

	Calculated for $C_9H_{16}(OAc)_2$.	Found.
C..........	64·5 per cent.	64·67 per cent.
H..........	9·1 ,,	9·45 ,,
O..........	26·4 ,,	25·88 ,,

As, however, a monacetyl-derivative of the composition $COMe\cdot[CH_2]_5\cdot CHMe\cdot OAc$ would have approximately the same composition (C = 66·0 per cent., H = 10·0 per cent., O = 24 per cent.). elementary analysis alone is not sufficient to prove beyond doubt that the compound is really a diacetyl derivative. As this point was of the utmost importance in deciding between the two possible formula for the reduction product, the quantity of acetic acid given on hydrolysis was determined. Three estimations of this kind were made; in each case, a weighed quantity of the pure compound was boiled with excess of standard potash, and the excess of alkali determined by titration with standard sulphuric acid, phenolphthalein being used as indicator.

The following results were obtained:—

I. 1·169 gram substance was boiled for 1⅓ hours with 150 c.c. of potash (1 c.c. = 0·00597 gram of $C_2H_4O_2$), and the cold solution titrated with sulphuric acid of the same strength; 56·4 c.c. of acid were required, showing that 93·6 c.c. of potash had been neutralised.

II. 0·8638 gram substance was boiled for two hours with 100 c.c. of potash, and the solution titrated with sulphuric acid; 44·3 c.c. of acid were required.

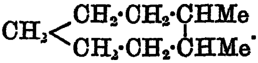
III. 0·5676 gram substance was boiled for an hour with 100 c.c. of potash, and the cold solution titrated; 54·7 c.c. of sulphuric acid were required.

	Calculated for $C_9H_{16}(OAc)_2$.	Found.		
		I.	II.	III.
$C_2H_4O_2$......	49·58 p. c.	47·8	48·4	47·6 p. c.

These results show conclusively that the compound in question is a diacetyl derivative, and, consequently, the presence of two hydroxy-groups in the original reduction product may be considered as proved.

Dimethylheptamethylene diacetate is a colourless, mobile liquid possessing a sweet, rather pleasant smell, and boiling at 199—202° under a pressure of 65 mm. It seems to be insoluble in cold water, but is readily soluble in alcohol, ether, acetic anhydride, and other organic solvents. It is readily hydrolysed even by very dilute aqueous potash, as is shown by the quantitative experiments referred to above.

Dimethylheptamethylene,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\cdot CHMe\\ | \\ CH_2\cdot CH_2\cdot CHMe\end{matrix}.$$

One of the most important facts that can be adduced in favour of the closed-chain formula for the reduction product of diacetylpentane is that, when treated with hydriodic acid and amorphous phosphorus at a high temperature, it is converted into a hydrocarbon of the molecular formula C_9H_{18}, which, from its method of formation must be a saturated compound. This hydrocarbon, dimethylheptamethylene, is obtained in the following way:—The pure glycol is first heated for about two hours at 100° in a flask provided with a reflux condenser, with excess of concentrated hydriodic acid, in order to convert it into the moniodide described above; this product is isolated in the usual manner, and then heated in sealed tubes at 230—260° for 8 to 10 hours with a large excess of hydriodic acid of sp. gr. 1·96, and a little amorphous phosphorus, about 4 grams only of the crude iodide being placed in each tube. When the tubes were opened, the hydrocarbon, which formed a lighter-coloured layer on the surface of the acid, was separated with the aid of a funnel, washed well with sodium carbonate, dried over potassium carbonate, and distilled. The thermometer rose at once to about 145°, and between 145° and 160° almost three-quarters of the crude product passed over; the liquid which then remained in the flask boiled at a very much higher temperature, and was not examined further, owing to its small quantity. The fraction boiling at 145—160° was then distilled two or three times over potassium, and finally a sample of the liquid boiling constantly at 153—154° was collected separately for analysis.

The results obtained were the following:—

0·1300 gram substance gave 0·4072 gram CO_2 and 0·1717 gram H_2O.

	Calculated for C_9H_{18}.	Found.
C..........	85·7 per cent.	85·42 per cent.
H..........	14·3 ,,	14·67 ,,

A vapour density determination carried out in Hofmann's apparatus, and employing aniline as the heating vapour, gave the following result:—

0·0782 gram substance gave 68 c.c. of vapour. Barometer = 748 mm. Difference of level 490 mm. Temperature of vapour 184°, and of air 11°.

	Calculated for C_9H_{18}.	Found.
V.D.	63	61·2

Two elementary analyses of a sample of the hydrocarbon from another preparation gave the following results:—

I. 0·1271 gram substance gave 0·3965 gram CO_2 and 0·1702 gram H_2O.

II. 0·1192 gram substance gave 0 3727 gram CO_2 and 0·1588 gram H_2O.

	Calculated for C_9H_{18}.	Found. I.	Found. II.
C	85·7 p. c.	85·08	85·14 p. c.
H	14·3 „	14·88	14·83 „

Dimethylheptamethylene is a colourless mobile, strongly refractive liquid with an odour very like that of light petroleum; it boils at 153° under the ordinary atmospheric pressure. It is insoluble in water, and in concentrated hydriodic acid, but is miscible with organic solvents in all proportions. It seems to be a very stable substance, but owing to the small quantity at our disposal, we have not been able to investigate its properties as completely as would be desirable. It is not acted on by concentrated hydriodic acid; when treated with concentrated nitric acid, a reaction soon sets in, heat is developed, and dense brown fumes are evolved, but the reaction soon slackens, and heat must be applied before complete solution ensues; as far as our experiments went, no compounds other than acids of low molecular weight are formed by the oxidation of the hydrocarbon in this way.

Condensation Product of Dimethyldihydroxyheptamethylene.

It has been mentioned above that in the preparation of dimethyldihydroxyheptamethylene there is formed in small quantities a liquid of considerably higher boiling point, which seemed to be a condensation product of the glycol. In order to investigate the nature of this compound, the residues obtained in several operations were united, and the liquid submitted to fractional distillation under a pressure of about 200 mm.; at first, a small quantity of dimethyldihydroxyheptamethylene passed over, and then the thermometer rose rapidly to about 300°, the remainder boiling almost constantly at 305—310°.

This high boiling liquid gave the following result on analysis:—

0·2011 gram substance gave 0·4143 gram CO_2, and 0·2082 gram H_2O.

	Calculated for $C_{18}H_{34}O_3$	Found.
C............	72·48 per cent.	72·6 per cent.
H............	11·41 „	11·4 „
O............	16·11 „	16·0 „

A molecular weight determination by Raoult's method in glacial acetic acid solution gave the following data:—

0·9116 gram substance dissolved in 43·1 grams acetic acid lowered the melting point 0·271, as a mean of two closely agreeing observations.

	Calculated for $C_{18}H_{34}O_3$.	Found.
M. W	298	305

This result shows that the compound in question has been formed by the condensation of two molecules of diacetylpentane, or its reduction product; the analysis given above agrees very well with the formula $C_{18}H_{34}O_3$, but not so well with the formula $C_{18}H_{32}O_3$, which would require 72·9 per cent. of carbon and 10·8 per cent. of hydrogen. Considering, also, that a large excess of sodium was invariably employed in the reduction of diacetylpentane, and that the only other product is the glycol $C_9H_{18}O_2$, it seems almost certain that the condensation product is formed from the glycol, and not from the ketone, according to the equation

$$2C_9H_{18}O_2 = C_{18}H_{34}O_3 + H_2O.$$

just as diethylene glycol is formed from two molecules of ethylene glycol with elimination of one molecule of water.

The condensation product of the heptamethylene derivative has no well-defined properties; it is an almost colourless, very thick oil, boils at about 305—310° (200 mm. pressure), and shows no signs of crystallising even when kept for months at the ordinary temperature, or for some hours in a freezing mixture. It is insoluble in water, but the ordinary organic solvents dissolve it in large quantities.

Heriot Watt College,
Edinburgh.

XXVI.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XIX. *Compounds of the Oxides of Phosphorus with Sulphuric Anhydride.*

By R. H. Adie, M.A.

1. R. Weber (*Ber.*, **20**, 86) describes a solid compound of sulphuric and phosphoric anhydrides, $P_2O_5,3SO_3$, which he prepared by distilling off in a sealed tube the excess of sulphur trioxide from a mixture of the two substances. It is decomposed at 30°.

2 As this appears to be the only compound of an oxide of phosphorus and sulphuric anhydride which has been described, I endeavoured to ascertain whether it might not be possible to prepare the compound $M_2O_3,2SO_3$, which is so very stable in the case of nitrogen, and has a definite existence in the case of arsenic, whilst in the cases of antimony and bismuth the trisulphate, $M_2O_3,3SO_3$, is formed.

The compounds of arsenic and antimony are directly obtained from the sesquioxide without oxidation, but in the case of nitrogen it is formed from nitric oxide, which, during the course of the reaction, becomes oxidised at the expense of the sulphur trioxide; consequently, I started with "acid phosphorous anhydrous," obtained from Messrs. Harrington Bros., Cork.

Quite recently, Thorpe and A. E. Tutton (Trans., 1890, **57**, 545) have prepared pure phosphorous anhydride, which differs from the above in several respects, since the latter melts only at a considerably higher temperature than 30°, is not decomposed by light at any rapid rate, and is instantly soluble in water; the acid obtained from Messrs. Harrington contains 65·1 per cent. of P_2O_3, and is, therefore, approximately H_3PO_3, which contains 67·1 per cent. of P_2O_3.

3. Anhydrous phosphorous acid dissolves quietly in concentrated sulphuric acid without forming an insoluble compound. The mixture when warmed gives off sulphur dioxide, and contains phosphoric acid only.

4. When anhydrous phosphorous acid was dropped into sulphur trioxide, there was a great development of heat, accompanied by the formation of sulphur dioxide and some sulphur. A blue, oily compound separated out in small quantity from the trioxide, which was itself coloured a fine indigo-blue. At the high temperature produced by the reaction, the phosphorous acid had reduced some of the trioxide

to sulphur, which dissolved in the trioxide to form blue sulphur sesquioxide.

In order to avoid the effect of the rise of temperature, the sulphur trioxide was distilled into a beaker to form a layer of about 2 mm. deep, which was then placed in a freezing mixture. The phosphorous acid was then carefully dropped, in small pieces, on the solid trioxide; as before, they united with violence, but formed no sulphur sesquioxide if the addition were gradual enough.

The compound remained liquid on the surface of the solid trioxide, and the contact and union of the phosphorous acid and the solid trioxide was seen to be accompanied by the liberation of a gas, which proved to be sulphur dioxide.

After the compound had remained in contact with the sulphur trioxide in the freezing mixture for some time, it was poured off and analysed. The results, which were fairly concordant, were as follows:—

	I.	II.	III.	IV.	V.	VI.
SO_3	53·47	54·36	—	—	—	—
P_2O_3	0·88	—	1·72	1·04	—	—
P_2O_5	—	—	—	—	34·54	30·19

	Calculated for		
	$P_2O_3,2SO_3$.	$P_2O_5,2SO_3$.	$H_3PO_4,3SO_3$.
SO_3	59·26	52·98	55·14
P_2O_3	40·74	—	—
P_2O_5	—	47·02	32·38

The phosphorous acid is almost completely oxidised, by the reduction of the trioxide in the cold, to sulphur dioxide, and, if warm, to sulphur dioxide and sulphur, forming the compound $H_3PO_4,3SO_3$.

5. The compound $H_3PO_4,3SO_3$ is a viscid liquid, generally coloured light-brown. It fumes in contact with the air, and dissolves in water with the development of heat, but without violence, forming sulphuric and orthophosphoric acids with only a trace of the pyro- and meta-acids. It is, on the whole, best represented as sulphonyl phosphate, $(SO_3H)_3PO_4$.

6. As phosphorous acid is so readily oxidised by sulphur trioxide, and as the lower oxides of phosphorus, with the exception of P_4O, are not well known, I next tried the action of phosphorus on sulphur trioxide.

When a piece of phosphorus is dropped into liquid sulphuric anhydride, it reduces the latter with violence to sulphur dioxide, and is itself oxidised, forming a white, flocculent solid floating in the liquid. When the pieces of phosphorus were large, the heat of combination raised the temperature of the phosphorus sufficiently high to ignite it.

It is difficult to free the solid from adhering trioxide, and at the same time to prevent its spontaneous ignition from the oxidation of finely divided globules of phosphorus disseminated throughout its mass. The trioxide requires to be near its boiling point for the reaction to take place, and this fuses the phosphorus.

The best way of obtaining a fairly pure product is to press out the phosphorus under water into a very thin plate, and then to drop pieces of this into the warmed trioxide. The reaction is violent, and frequently accompanied by a rain of sparks of burning phosphorus. When the reaction is complete, the trioxide is boiled, and the compound raked out on a warm, dry porous tile, which is placed in a desiccator over phosphoric anhydride in a warm place in the dark for two to three hours. The product can then be placed in a weighing bottle.

I have tried manipulating in an atmosphere of carbonic anhydride, but got no better results. Distilling the excess of trioxide from the compound is not a successful operation, as oxidation occurs just when the trioxide is gone. The solvents of phosphorus decompose the substance, and the method which seems to give the best results is to work at a low temperature in a dry atmosphere.

Heating phosphorus with sulphur trioxide in a sealed tube not only oxidises all the phosphorus, but converts it at once into phosphoric anhydride, which forms a clear solution in the trioxide.

The product prepared as above gave the following results on analysis :—

	I.	II	III.	IV
P	35·03	32·33	—	—
SO_3	—	33·85	30 83	—
P_2O_3......	—	—	—	35·93

	Calculated for		
	P_2O_3,SO_3.	P_2O_4,SO_3.	$3P_2O_4,2SO_3$.
P	32·63	30·10	34·57
SO_3	42·10	38·82	29·75
P_2O_3	57·89	30·58	35·12

The compound which must be represented as $3P_2O_4,2SO_3$ decomposes on standing for 2—3 weeks over phosphoric anhydride in air into P_2O_5 and SO_2. The same change occurs when the substance is heated without sulphur trioxide to a temperature of about 55—60°; in this case the sulphur dioxide is given off in bubbles from the frothy mass. It is to be noted that $P_2O_5,3SO_3$ decomposes at 30°. It is darkened very rapidly by light, which is rather more characteristic of P_2O_3 than of P_2O_4. It is instantly decomposed by water, but the phosphorus-containing part dissolves only very slowly, which is also characteristic of P_2O_3, and not of P_2O_4, which dissolves immediately.

The group sulphate $P_2O_3,2SO_3$, then, is not formed by this reaction, nor by any conditions attainable at present, its place being taken by the above compound, $3P_2O_4,2SO_3$.

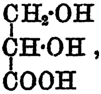
I have much pleasure in acknowledging the assistance of Mr. Pattison Muir, to whom I am indebted for the use of the laboratory of Gonville and Caius College during this work.

XXVII.—*Crystalline Form of the Calcium Salt of the New Optically Active Glyceric Acid.*

By Alfred E. Tutton, Assoc. R.C.S., Demonstrator in Chemistry at the Royal College of Science, London.

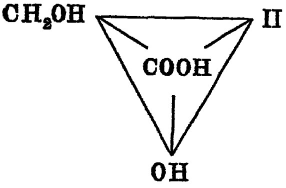
In a recent communication (this vol., p. 96) by P. F. Frankland and W. Frew, it was shown that when calcium glycerate was submitted to the fermenting action of the *Bacillus ethaceticus* one half only of the glyceric acid was destroyed, and that the remaining half was optically active, rotating the plane of polarisation to the right. In view of the fact that in every case hitherto investigated, where an inactive compound has been separated into two complementary optically active varieties, the phenomenon of hemihedrism has been manifested in the crystals of the compounds themselves, or, in the case of uncrystallisable acids, in their salts, it was important to submit the best crystallisable salt of this optically active glyceric acid to a thorough crystallographical investigation. An additional chemical interest attaches to such investigations since the appearance of the paper communicated to the *Berichte* (1891, p. 101) by Fock, in which a theory of optical activity is discussed, attempting, on the lines of the Van t'Hoff-Wislicenus hypothesis, to account for this invariable occurrence of hemihedrism. Generally, as in the case of the salts of dextro- and lævo-tartaric acids, the two oppositely active modifications are strictly isomorphous, exhibiting precisely the same forms, and, where those forms are completely developed, the same angles; but only half of the faces corresponding to several of these forms are developed, the half shown by one variety being absent from the other, and *vice versâ*. In other words, the crystals are complementarily hemihedral, being generally related in the same way that an object is to its mirror-image.

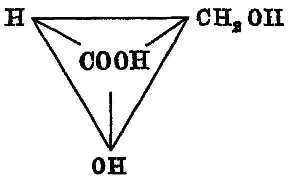
It is now generally admitted by crystallographers that this mode of manifestation of hemihedrism is determined by differences in the internal arrangement of the atoms or groups in the molecules themselves of the two varieties. Glyceric acid,



$$\begin{matrix}CH_2{\cdot}OH\\ |\\ CH{\cdot}OH\\ |\\ COOH\end{matrix}$$

, has manifestly one so-called asymmetric carbon atom, that belonging to the CHOH group. There are consequently two possible arrangements of the molecule in space, probably corresponding to the two optically active varieties





The new dextro-glyceric acid itself is an uncrystallisable syrup, but the calcium salt, $Ca(C_3H_5O_4)_2,2H_2O$, has been obtained in crystals sufficiently well formed to admit of a complete investigation. Although the acid itself is dextro-rotatory, aqueous solutions of this calcium salt are lævo-rotatory to the extent $[\alpha]_D = -12{\cdot}09$.

The crystals examined were colourless, well-formed prisms eminently suitable for goniometrical purposes, obtained by the slow evaporation of an aqueous solution. The crystals ordinarily obtained by rapid evaporation exhibit precisely the same faces, but the reflections usually observed are not quite so perfect as those given by the crystals obtained by slow evaporation. The prisms were perfectly terminated at both ends by pyramid and dome forms. The larger ones were about 5 mm. long, and 2 mm. by 1·5 mm. in section. One prism was observed nearly 1 cm. in length.

System: monoclinic, hemihedral. Habit: prismatic; $\beta = 69^\circ\ 6'$
Ratio of axes: $a : b : c = 1{\cdot}4469 : 1 : 0{\cdot}6694$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $c = \{001\}oP$; $r' = \{\bar{2}01\} + 2\bar{P}\infty$;
$p = \{110\}\infty P$; $m = \{011\}\not{P}\infty$; $o = \{111\} - P$; $s = \{\bar{1}\bar{1}1\} + P$;
$n = \{\bar{2}\bar{1}1\} + 2\bar{P}2$.

The usual appearance of the crystals is seen in Fig. 1. which is drawn from the calculated elements. Fig. 2 represents their spherical projection upon the symmetry plane. Those poles which are represented by rings are situate upon the hemisphere lying beneath the plane of projection; those represented by dots are situate upon the upper hemisphere.

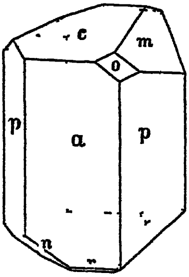


FIG. 1.

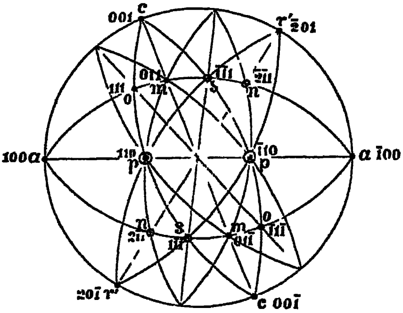


FIG. 2.

The faces of the forms $o\{111\}$ and $m\{011\}$ were never found developed upon the left side of the symmetry plane, but only upon the right. The faces of $s\{\bar{1}\bar{1}1\}$ and $n\{\bar{2}\bar{1}1\}$ were, conversely, never found developed upon the right, only upon the left of the plane of symmetry. The crystals are therefore undoubtedly hemihedral, the two extremities of the symmetry axis b being terminated in an entirely different manner.

The best developed face is the orthopinacoid $a\{100\}$, the prisms being frequently tabular upon it. The prism faces $p\{110\}$ are always well developed. It was frequently noticed that the right-hand faces (110) and ($\bar{1}10$) of this form were much more brilliant and evenly developed than those on the left hand, ($1\bar{1}0$) and ($\bar{1}\bar{1}0$), which were often curved and of dull appearance, resembling the faces $s\{\bar{1}\bar{1}1\}$ and $n\{\bar{2}\bar{1}1\}$ in this respect. This mode of manifestation of hemihedrism corresponds to that in the case of cane-sugar, whose prism faces on the two sides of the symmetry plane yield different corrosion figures. No trace of the clinopinacoid $b\{010\}$ was observed. The face chosen as the basal plane $c\{001\}$ is usually the most prominent of the faces perpendicular to the symmetry plane, but occasionally the orthodome $r'\{\bar{2}01\}$ is equally well developed. The hemiclinodome $m(011)$ is always a prominent face on the right side of the symmetry plane, and the neighbouring pyramid face $o(111)$ is generally relatively developed to about the extent shown in the drawing. The pyramid faces $s(\bar{1}\bar{1}1)$ and $n(\bar{2}\bar{1}1)$ upon the left side of the symmetry plane differ greatly in character from the faces m and o at the right side, seldom giving good reflections owing to dulness and curvature. The monoclinic, and not triclinic, nature of the crystals is proved by the presence of a complete prism zone, the four faces of which are symmetrically disposed in respect to the two orthopinacoid faces; by the fact that the zone of the faces *a*(100), *c*(001), and *r*′($\bar{2}01$) is perpendicular to the prism zone and to the plane of symmetry exhibited by the latter zone; and, conclusively, by the optical properties hereafter described.

Following is a table exhibiting the results of the angular measurements obtained with the large Fuess goniometer from 12 crystals selected from two distinct crops of crystals.

Angle measured.	No of measurements.	Limits.	Mean observed	Calculated.
$ap = 100 : 110$	42	52° 32′— 51° 16′	53° 29′	*
$pp = 110 : \bar{1}10$	20	72 7 — 73 33	73 4	73° 2′
$ac = 100 : 001$	13	68 22 — 69 42	69 3	69 6
$cr' = 001 : \bar{2}01$	13	52 4 — 52 31	52 13	*
$r'a = \bar{2}01 : \bar{1}00$	13	58 35 — 58 46	58 11	*
$cm = 001 : 011$	10	31 47 — 32 19	32 3	32 2
$r'n = \bar{2}01 : \bar{2}\bar{1}1$	2	29 43 — 29 48	29 45	29 47
$ao = 100 : 111$	7	53 59 — 54 10	54 3	53 54
$om = 111 : 011$	7	18 20 — 18 35	18 26	18 29
$ma = 011 . \bar{1}00$	13	107 22 —108 24	107 41	107 37
$an = \bar{1}00 : \bar{2}\bar{1}1$	11	62 32 — 63 44	63 6	63 10
$ns = \bar{2}\bar{1}1 : \bar{1}\bar{1}1$	1	—	21 35	21 27
$sa = \bar{1}\bar{1}1 : 100$	3	94 49 — 95 34	95 18	95 23
$po = 110 : 111$	9	43 51 — 44 44	44 35	44 38
$oc = 111 : 001$	9	32 56 — 33 15	33 7	33 7
$cs = 001 : \bar{1}\bar{1}1$	7	41 32 -- 43 2	42 10	42 17
$sp = \bar{1}\bar{1}1 : \bar{1}\bar{1}0$	7	59 15 — 60 54	59 59	59 58
$pc = \bar{1}\bar{1}0 : 00\bar{1}$	14	77 2 — 78 21	77 52	77 45
$cp = 00\bar{1} : 110$	16	101 39—103 36	102 16	102 15
$pm = 110 : 011$	9	52 15 — 53 25	52 42	52 41
$mn = 011 : \bar{2}\bar{1}1$	5	79 5 — 79 26	79 15	79 12
$np = \bar{2}\bar{1}1 : \bar{1}\bar{1}0$	5	47 41 — 48 23	48 1	48 7
$pr' = 110 . \bar{2}01$	14	106 35 — 108 42	108 5	108 1
$r'p = \bar{2}01 : \bar{1}\bar{1}0$	26	70 51 — 73 32	71 55	71 59
$ps = \bar{1}\bar{1}0 : 1\bar{1}\bar{1}$	5	66 42 — 67 17	67 4	67 5
$sr' = 1\bar{1}\bar{1} : 20\bar{1}$	6	40 36 — 41 29	41 5	40 56
$pm = \bar{1}10 : 011$	3	75 5 — 76 21	75 37	75 45

The angles marked with an asterisk were chosen as the basis of the calculations, *ap* on account of the large number of measurements obtained owing to the recurrence of this angle four times upon each perfectly-developed crystal, and *cr*′ and *r*′*a* on account of the greater relative agreement of the measured values of these angles. It may be remarked that the mean observed values given in the table agree very closely with the measurements afforded by one exceptionally perfect crystal.

There is a moderately good cleavage parallel to the basal plane

$c(001)$, and the prisms are consequently very apt to break across in this direction. The cleavage plates are usually very rough, however.

Optical Properties.—The extinctions upon the face $a(100)$ are parallel to the prism edges. A section cut parallel to $b(010)$, the symmetry plane, extinguishes obliquely to the prism edges, the direction of extinction making an angle of 23° with those edges, almost perpendicular to the basal plane $c(001)$. In convergent light, this section shows no rings in air; but in oil, the two optic axes and their systems of rings are observed separated at an extremely large angle, evidently the obtuse angle. The first median line is therefore almost perpendicular to the basal plane. Upon cutting a section parallel to the basal plane $c(001)$, both axes and their rings are well seen in air separated at their acute angle, and lying symmetrically on either side of the symmetry plane.

Hence, the plane of the optic axes is perpendicular to the symmetry plane $b(010)$, and the first median line makes an angle of 23° with the vertical axis c, thus emerging almost normal to the basal plane $c(001)$. The type of dispersion is horizontal, and the hyperbolic brushes are bordered with blue inside, hence the dispersion is of the nature $\rho < v$.

Sections require to be about 1 mm. thick in order to show the rings well, owing to the low specific refractive power.

The following mean values for the apparent acute angle in air 2E, the apparent acute angle in oil 2H*a*, and the apparent obtuse angle in oil 2H*o*, were obtained with the Fuess optic axial angle apparatus:—

	2E.		2H*a*.		2H*o*.	
Lithium light........	51°	35′	35°	10′	147°	25′
Sodium light........	52	30	35	40	146	40
Thallium light.......	53	50	36	30	145	55

From these observed values, the true acute angle between the optic axes 2V*a*, calculated by means of the formula $\tan Va = \dfrac{\sin Ha}{\sin Ho}$ is found to be as follows:—

For lithium light, 2V*a* = 34° 56′
„ sodium light 35 28
„ thallium light, 36 16

The mean refractive index β, calculated from the formula $\beta = \dfrac{\sin E}{\sin Va}$, is represented by the following numbers:—

$\beta_{Li} = 1{\cdot}4496.$
$\beta_{Na} = 1{\cdot}4521.$
$\beta_{Tl} = 1{\cdot}4545.$

The sign of the double refraction, as determined by means of a quarter undulation mica plate, is positive.

The optical properties thus completely bear out the monosymmetric nature of the crystals. Hence, this optically active calcium glycerate must be added to the list of optically active substances whose crystals are also hemihedral, a list which includes all the hitherto well-investigated cases.

XXVIII.—*Volumetric Estimation of Tellurium.* Part II.*

By Bohuslav Brauner, Ph.D., Professor in the Bohemian University,
late Berkeley Fellow of Owens College.

Third Method.

It is known that alkaline solutions of tellurium dioxide (alkaline tellurites) are converted into tellurates on treatment with chlorine (Berzelius, *Ann. Phys. Chem.*, **32**, 23), but according to Oppenheim (*J. pr. Chem.*, **71**, 266) the reaction proceeds only very slowly.

The reaction with iodine I found to take place, as I expected it would do, in accordance with the following equations:—

I. $Na_2TeO_3 + I_2 + 2NaHCO_3 = Na_2TeO_4 + 2NaI + 2CO_2 + H_2O$, or

II. $Na_2TeO_3 + I_2 + 2NaOH = Na_2TeO_4 + 2NaI + H_2O$.

When a solution of iodine in potassium iodide is added to a solution of normal sodium tellurite to which some starch paste has been added, the very first drop of the solution produces an intense blue coloration, which, however, disappears in a short time, and this effect is reproduced on every fresh addition of iodine, showing that the oxidation with iodine is but slow. At first the tellurous acid is easily converted into telluric acid by the excess of iodine, but the rate of conversion becomes slower with the increase of the amount of telluric acid formed, so that even after a considerable excess of iodine has acted for 24 hours, part of the tellurous acid remains unchanged. As, however, in several experiments, it was found that the theoretical quantity of iodine solution was required for the oxidation of weighed quantities of tellurium dioxide in solution as tellurite, the conclusion must be drawn that part of the iodine entered into reaction with the sodium hydrogen carbonate always present.

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* Compare Part I, this vol., pp. 58—67.

When the action of iodine takes place at the temperature of the water-bath, the oxidation to telluric acid takes place much more rapidly. In order to study this phenomenon, solutions of weighed quantities of tellurium dioxide, in the least possible quantity of caustic soda, were treated with iodine solution on a water-bath until no further decolorisation of the iodine solution took place. Under these circumstances the oxidation was usually found to be complete after heating for 10 to 15 minutes, if an excess of iodine was used, twice or thrice that necessary for the conversion. The experiments must, of course, be carried on in closed vessels in order to avoid loss of iodine by evaporation. It might be expected that this mixture of sodium tellurate with potassium iodide, sodium iodate, and free iodine, after cooling, would yield all the free iodine which was not spent on the oxidation, on being decomposed with dilute hydrochloric acid added in slight excess, since telluric acid does not immediately yield free iodine when treated with dilute hydrochloric acid in presence of potassium iodide.

When the experiment is carried out in the manner described, namely, by heating the tellurite with an excess of iodine solution and, after cooling, adding dilute hydrochloric acid to distinctly acid reaction, iodine is set free, but on determining the amount by means of standardised thiosulphate, and subtracting the iodine found in this way from the total added, it is always found that a larger amount of free iodine has disappeared than corresponds with the theoretical, and that the results vary greatly. If, after decolorisation with thiosulphate more hydrochloric acid is added, iodine is again set free, which is decolorised on adding more thiosulphate, and on repeating this operation until much acid had been added, a peculiar pale-brown coloration is produced which is not removed by thiosulphate, so that the end of the reaction becomes indistinct.

The above is the result of a series of more than 30 experiments which were made under most varied conditions, but I have omitted all superfluous details as the method was so unsatisfactory.

This method, although simple in principle, is yet inapplicable to the estimation of tellurous acid, for the following reasons:—

(1.) Because the oxidation by iodine proceeds but very slowly in the cold.

(2.) Even when it is completed by heating at 100°, it is impossible to determine exactly the excess of iodine employed.

Fourth Method.

After finding that the conversion of tellurous into telluric acid by chromic acid in hydrochloric acid, or by iodine in alkaline solution, proceeds only very slowly, I directed my attention to a more powerful oxidising agent, namely, potassium permanganate.

Experiments in Hydrochloric Acid Solution.

It might be expected, from the analogy of tellurium to antimony, that in hydrochloric acid the following reaction would take place:—

III. $2KMnO_4 + 6HCl + 5TeO_2 = 2KCl + 2MnCl_2 + 3H_2O + 5TeO_3$.

It was found, however, that on adding potassium permanganate solution to one of tellurium dioxide in hydrochloric acid, the liquid became brown from the manganic chloride formed, and the solution had a strong smell of chlorine. At the same time tellurous acid is converted into telluric acid, and the end of the reaction is marked by a peculiar red-brown coloration due to the excess of permanganate. As might be inferred from the analogy to the behaviour of tellurous solutions in sulphuric acid (see below, VII), the reaction corresponds with the following equation:—

IV. $2KMnO_4 + 8HCl + 4TeO_2 = 2KCl + Mn_2Cl_6 + 4H_2O + 4TeO_3$.

The manganic chloride is without action on tellurous and telluric acids, but it may be destroyed by the addition of ferrous sulphate.

V. $MnCl_3 + FeSO_4 = MnSO_4 + FeCl_3$.

The excess of ferrous salt added is determined with permanganate.

For the experiments, an approximately decinormal solution of permanganate was used, which was standardised by decinormal oxalic acid, also a solution of ammonium ferrous sulphate of equal strength; the volumes of ferrous solution and of permanganate are then calculated, so that they are expressed as decinormal solutions, after which on subtraction of the number of c.c. of ferrous solution from that of the permanganate, the volume of the latter, which was used for oxidation, is found. From this the quantity of tellurium dioxide can be calculated as if the reaction corresponded with the equation III. As every c.c. of decimal permanganate contains 0·0008 gram of available oxygen, 0·00798 gram $TeO_2 = \frac{1}{20000}$ mol. wt., is indicated by it. The solution always contained some sulphuric acid in order to avoid the separation of tellurous acid on dilution with water.

No. of expt.	$KMnO_4$ added.	$FeSO_4$ back.	$KMnO_4$ for oxid.	HCl.	H_2O.	TeO_2 taken.	TeO_2 found.	TeO_2.
	c.c.	c.c.	c.c.	c.c.	c.c.	gram.	gram.	p.c.
1	23·45	8·04	15·41	1	10	0·1020	0·1230	120·6
2	22·55	8·77	13·78	1	100	,,	0·1100	107·8
3	20·65	7·04	13·61	1	150	,,	0·1086	106·5
4	21·31	8·04	13·27	1	150	,,	0·1059	103·8
5	21·21	8·04	13·17	1	150	,,	0·1051	103·0
6	20·45	7·04	13·41	1	200	,,	0·1071	105·0
7	20·11	8·41	11·70	3	50	0·0828	0·0934	112·8
8	21·23	10·28	10·95	3	100	,,	0·0874	105·5
9	20·16	9·35	10·81	3	150	,,	0·0863	104·2
10	20·23	9·35	10·88	3	200	,,	0·0868	104·9
11	20·21	9·35	10·86	3	250	,,	0·0867	104·7

From this series of experiments it follows that the volume of permanganate used for oxidation is always higher than the theoretical, and that the quantity increases with the amount of hydrochloric acid present, or, generally with increasing concentration of the solution. When much water is present, a little more still is required to produce the coloration.

When ferrous sulphate is added to the tellurous solution before the titration, no manganic chloride is formed on adding the permanganate, but nevertheless evolution of chlorine takes place (compare Exp. 12 and 13), so that the results are again too high. The addition of manganous sulphate—as used with good effect by Kessler and by Zimmerman in estimating iron in hydrochloric solutions—gives a slightly better result, but the end of the reaction is indistinct, as the coloration appears only for a moment.

No. of expt.	$KMnO_4$ added.	$FeSO_4$ back.	$KMnO_4$ for oxid.	HCl.	H_2O.	TeO_2 taken.	TeO_2 found.	TeO_2.
	c.c.	c.c.	c.c.	c.c.	c.c.	gram.	gram.	p.c.
12	29·85	16·08	13·77	1	100	0·1020	0·1100	107·8
13	29·85	16·08	13·77	1	100	,,	0·1100	107·8
14	21·21	8·04	13·17	1	100*	,,	0·1051	103·0

It is impossible to obtain constant results even at the same degree of concentration, as higher or lower numbers are obtained, according to whether the permanganate is poured in quickly or slowly.

Experiments in Sulphuric Acid Solution.

Here again, the reaction between potassium permanganate and a

* And 15 c.c. $MnSO_4$ (1 : 5).

solution of tellurium dioxide in sulphuric acid does *not* correspond with the "normal" equation—

$$\text{VI.}\quad 2KMnO_4 + 3H_2SO_4 + 5TeO_2 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5TeO_3,$$

but it is represented by

$$\text{VII.}\quad 2KMnO_4 + 4H_2SO_4 + 4TeO_2 = K_2SO_4 + Mn_2(SO_4)_3 + 4H_2O + 4TeO_3,$$

for the manganic sulphate formed as the first reduction product of the permanganate is unable to oxidise the tellurous acid.

I have studied the action of sulphuric acid of varying concentration on tellurium dioxide more fully, but only the following facts are of interest in connection with the present paper.

Finely powdered tellurium dioxide is only slowly, and with difficulty, dissolved by dilute sulphuric acid, even on boiling, when it is observed that any excess of the dioxide is converted into the "octahedral" (*i.e.*, tetragonal) modification, measurable crystals of which were first obtained by the author. The solution in sulphuric acid of 20 per cent. contains 0·7 per cent. TeO_2, an acid of 30 per cent. 0·85 per cent. TeO_2, and an acid of 50 per cent contains 4·4 per cent. of its own weight of TeO_2 in solution. All these solutions are considerably "supersaturated," and after some time the substance in solution is deposited from them. From the dilute acid solutions, the above-mentioned quadratic octahedra separate, whilst, from concentrated solutions, beautiful and extremely complicated rhombic crystals of the basic sulphate, $2TeO_2,SO_3$, are obtained. In order to prepare a tolerably stable solution, about 30 parts of dilute sulphuric acid (1 : 1) must be taken for one part of tellurium dioxide, and even then, to avoid separation of crystals, the solution must not be allowed to stand for long before titration. As the solution takes place very slowly, the finely powdered dioxide must be shaken while warming the acid, in order to avoid the formation of crystalline crusts of the dioxide.

On the addition of permanganate to such a solution, the first drops produce a brown coloration, due to the formation of manganic sulphate, and on adding more this becomes darker, until an excess of unaltered permanganate, indicated by a red-brown colour, shows that enough has been added to complete the reaction.

If the reaction really corresponds with equation VII, the quantity of permanganate used, compared with the quantity calculated from the equation VI, must be in the proportion of 5 : 4, as in the case VII, 7 mols., in the case VI, 5 mols., are oxidised by one and the same quantity of permanganate. This has been proved by the following:—

Exp. 15.—0·1508 gram of TeO_2 requires, according to VI, 18·9 c.c. of decinormal permanganate, but, according to VII, 18·9 × $\frac{5}{4}$ = 23·6 c.c. Under the above conditions of experiment, the red coloration, showing an excess of permanganate as well as its characteristic absorption spectrum, was seen when 23·8—24 c.c. had been added. A series of analogous experiments gave a similar result, proving that the reaction really corresponds with the equation VII.

Titrating back with Ferrous Sulphate.—On adding permanganate to the sulphuric acid solution of tellurium dioxide, an evolution of ozonised oxygen is observed, and the red-brown solution becomes, after a few minutes, turbid. This turbidity, due to the separation of manganic hydrate, takes place later, when the solution contains a larger excess of free sulphuric acid. In order to destroy the higher manganese compounds, a decinormal solution of ammonium ferrous sulphate, containing some free sulphuric acid was added, until the solution became clear and colourless, after which the excess of ferrous salt was titrated in the usual way by permanganate. After subtracting the volume of permanganate corresponding with the ferrous salt (col. III), from the total permanganate added (col. II), the volume of decinormal permanganate used for the oxidation of tellurium dioxide is obtained (col. IV).

No. of expt.	$KMnO_4$ added.	$FeSO_4$ back.	$KMnO_4$ for oxid.	TeO_2 taken.	TeO_2 found.	TeO_2.
	c.c.	c.c.	c.c.	gram.	gram.	p.c.
15	27·11	9·10	18·01	0·1418	0·1437	101·4
16	26·06	8·04	18·02	„	0·1437	101·4
17	25·96	8·04	17·92	„	0·1430	100·9
18	25·96	8·04	17·92	„	0·1430	100·9
19	20·94	7·93	13·01	0·1020	0·1038	101·8
20	21·74	8·92	12·82	„	0·1023	100·3
21	32·67	19·83	12·84	„	0·1025	100·5
22	19·96	8·20	11·76	0·0910	0·0940	100·0
23	19·15	7·18	11·97	„	0·0955	101·6
24	19·12	7·18	11·94	„	0·0953	101·4
25	19·05	7·18	11·87	„	0·0947	100·8
26	19·03	7·18	11·85	„	0·0946	100·6
					Mean....	101·0

As a mean, 1 per cent. of tellurium dioxide is found, over and above the quantity taken for the experiment, as 1 per cent. of the available oxygen of the permanganate escapes as free ozonised oxygen. The experimental errors are, of course, larger the smaller the quantity of dioxide taken.

Titrating back with Oxalic Acid.—The method becomes more elegant when, instead of the ferrous salt, decinormal oxalic acid is used for the destruction of the manganic compound formed. For, firstly, one and the same solution may be used both for the destruction of the manganic salt and for standardising the permanganate;* secondly, an absolutely colourless solution is obtained after the decomposition of the brown manganic compound, so that the end of the reaction becomes far more sharp than when the ferrous salt is used; and lastly, oxalic acid is preferable to the easily oxidisable ferrous salt, on account of its stability.

On carrying out the analysis, decinormal permanganate is added to the telluro-sulphuric solution in notable excess, which is—after some practice—easily distinguished by the colour of the brown solution, and then, from a second burette, decinormal oxalic acid is run in quickly in quantity more than one-third and less than one-half the volume of the decinormal permanganate which has been added. The solution becomes completely decolorised, either at once or after gently warming. The liquid is then heated to about 60°, after which permanganate is again added from the first burette in slight but distinct excess, and the volume of decinormal permanganate used for the oxidation of the tellurium dioxide is obtained after expressing the total added as decinormal, and subtracting the volume of decinormal oxalic acid added. The weight of tellurium dioxide (col. VI) is obtained on multiplying the c.c.'s of decinormal permanganate by 0·00798 gram (log. = 7·90200).

It should be added, that, according to direct experiments, telluric acid remains unchanged, not only on warming with dilute sulphuric and decinormal oxalic acid to 60°, but also even on boiling for five minutes.

The following series of experiments (p. 246) show the manner in which sulphuric solutions of tellurium dioxide behave towards permanganate when its excess is titrated back with oxalic acid.

It is seen, from the following series of experiments, that the quantity of decinormal permanganate which oxidises tellurous to telluric acid, in sulphuric acid solution, equals, as a mean, 101·1, when the theoretical quantity is taken as = 100. The surplus of 1·1 per cent. permanganate used is explained by the evolution of free oxygen which escapes in the ozonised form while the permanganate is flowing into the tellurous solution. The following experiment confirms the fact that evolution of gaseous oxygen really takes place during the reaction. The wide glass tube *a*, of about 100 c.c. capacity, is furnished on its upper part with a glass stopcock, *b*, and a funnel, *c*. The continuation of the lower narrow part *d*, forms a capillary tube *ee*. To this, on its upper end, a thin, wide rubber tube, *f*, is joined. At first the capillary and the rubber tubes are filled with water, after which both ends of the rubber tube are closed by clamps or ligatures *g* and *h*. Then, through the funnel *c*, the sulphuric solution of tellurium is poured into the wide tube *a*, and then some water containing sulphuric acid on to the surface. At last a solution of permanganate is poured in cautiously, so that the whole tube is filled with the liquid, and part of it reaches into the funnel *c*.

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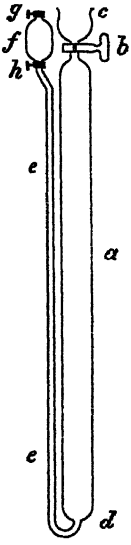
* On dissolving 16 grams of permanganate in 5 litres of water and decanting the solution, which has stood for some days, from the manganese oxides separated, a solution was obtained, 19 8 c.c. of which were found equivalent to 20 c.c. of decinormal oxalic acid. This relation remains unaltered for months, when the solutions are kept in the dark.



After closing the stopcock *b*, and opening the tap or ligature at *h*, the tellurous solution is mixed with the permanganate by inclining the apparatus. At this moment a contraction takes place, and the water contained in *f* runs into the tube *a*, in order to fill the vacuum. Without the above arrangement, air would rush into the apparatus through the joints. After the liquids have been mixed, numerous gas bubbles are evolved in the liquid, and after some time collect underneath the stopcock *b*, and, at the same time, part of the liquid contained in *a* escapes through the capillary *ee* into *f*, so that this wide, soft rubber tube acts in the beginning, and at the end of the experiment, as a reservoir in opposite senses.

On filling *c* with water and collecting the evolved gases in a small eudiometer by opening the stop-cock, *b*, it is easily shown that it consists principally of oxygen (a little nitrogen present is due to the air in the liquids originally employed).

No. of expt.	$KMnO_4$ added.	$C_2O_4H_2$ back.	$KMnO_4$ for oxid.	TeO_2 taken.	TeO_2 found.	TeO_2.
	c.c.	c.c.	c.c.	gram.	gram.	p.c.
27	33·5	15·0	18·5	0·1463	0·1476	100·9
28	33·5	15·0	18·5	,,	0·1476	100·9
29	26·6	11·9	14·7	0·1166	0·1173	100·6
30	24·7	9·95	14·75	,,	0·1177	100·9
31	26·25	11·55	14·7	,,	0·1173	100·6
32	29·07	10·0	19·07	0·1508	0·1522	100·9
33	25·45	6·3	19·15	,,	0·1528	101·3
34	25·3	6·3	19·0	,,	0·1516	100·5
35	20·83	8·0	12·83	0·1020	0·1024	100·4
36	20·93	8·0	12·93	,,	0·1032	101·2
37	20·97	8·0	12·97	,,	0·1035	101·5
38	21·43	8·5	12·93	,,	0·1032	101·2
39	21·43	8·5	12·93	,,	0·1032	101·2
40	17·89	6·0	11·89	0·0940	0·0949	100·9
41	47·68	16·0	31·68	0·2501	0·2528	101·1
42	42·25	15·0	27·25	0·2163	0·2175	100·5
43	42·67	15·0	27·67	0·2191	0·2208	100·8
44	29·74	10·87	18·87	0·1487	0·1506	101·3
45	27·83	8·89	18·94	,,	0·1511	101·6
46	29·83	10·87	18·96	,,	0·1513	101·7
47	74·28	23·21	51·07	0·4033	0·4075	101·0
48	46·23	15·0	31·23	0·2460	0·2500	101·3
49	60·51	23·0	37·51	0·2956	0·2993	101·3
50	20·44	7·0	13·44	0·1053	0·1073	101·8
51	20·40	7·0	13·40	,,	0·1069	101·5
52	29·45	16·0	13·45	,,	0·1073	101·8
53	26·39	13·0	13·39	,,	0·1069	101·4
54	37·73	14·0	23·73	0·1880	0·1894	100·7
					Mean ..	101·1

The volume of the gas is but small, as, on oxidation of 1·596 gram. TeO_2 ($\frac{1}{100}$ of gram., mol. weight), only 0·0016 gram. of oxygen or 1·119 c.c. are evolved. In quantitative experiments, a somewhat larger volume was always found, owing to the reasons stated below.

It is not easy to explain this evolution of free oxygen and ozone. It may be assumed that part of the nascent oxygen atoms of permanganate unite to molecules before they find time for oxidising the tellurous acid. Another probable explanation is that this evolution of free oxygen is due to the decomposition of the unstable manganic sulphate formed. In order to throw some light on this process, an attempt was made to vary the conditions of the experiment in such a way that the evolution of oxygen was larger than 1·1 per cent.

Exp. 55 was made in the normal way, and gave a normal result. In Exp. 56, the permanganate was added to a hot tellurous solution; in Exp. 57, the whole volume of permanganate was mixed at once with the tellurous solution; in the Exps. 58, 59, and 60, the oxidised tellurous solution had stood for three hours in the dark, with the permanganate added, before titrating back with oxalic acid; Exp. 61 was made at a boiling heat.

No. of expt.	$KMnO_4$ added.	C_2O_4H back.	$KMnO_4$ for oxid.	TeO_2 taken.	TeO_2 found.	TeO_2
	c.c.	c.c.	c c.	gram.	gram.	p.c.
55	30·61	10	20·61	0·1627	0·1645	101·1
56	31·89	10·92	20·97	,,	0·1673	102·9
57	40·0	19	21·00	,,	0·1676	103·0
58	36·95	12	24·95	0·1845	0·1991	107·9
59	36·56	12	24·56	,,	0·1960	106·2
60	47·17	23	24·17	,,	0·1939	104·5
61	36·40	13	23·40	,,	0·1867	101·2

From the results of these experiments, it follows that the evolution of free oxygen is connected with the formation of the unstable manganic sulphate, which is decomposed with evolution of oxygen. As regards the further explanation of this evolution of oxygen, I must refer to the influence of different quantities of sulphuric acid on the action (Exps. 64—79).

Could the experiments be carried out under such conditions that the formation of the manganic salt could be avoided, it might be expected that the evolution of free oxygen would be lessened.

Now ferrous sulphate and oxalic acid destroy the manganic salts at the moment of their formation. Especially notable is the behaviour of oxalic acid, which, at the ordinary temperature, remains for some minutes unchanged when mixed with potassium permanganate in the presence of sulphuric acid; but on adding oxalic acid to a solution of tellurium dioxide in sulphuric acid, and then permanganate drop by drop, complete decolorisation takes place, and this effect is produced the quicker the more sulphuric acid is present, so that a permanent coloration shows that both the telluric and oxalic acids are oxidised. The same takes place in the presence of ferrous sulphate, so that the processes are represented by the following equations:—

VIII. $4TeO_2 + H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 4TeO_3 + K_2SO_4 + 2MnSO_4 + 2CO_2 + 4H_2O$, and

IX. $4TeO_2 + 2FeSO_4 + 2KMnO_4 + 4H_2SO_4 = 4TeO_3 + K_2SO_4 + 2MnSO_4 + Fe_2(SO_4)_3 + 4H_2O$.

On carrying out the experiments, practically no formation of manganic sulphate takes place, but, strange to say, the evolution of free oxygen is not prevented. This is proved by the Exps. 64, 65, 66, and 67, in which this method was used, and, further, by the two following (p. 248).

Exp. 21 gave a similar result where the titration was done in the presence of ferrous sulphate

It is seen that the evolution of oxygen takes place, even in the

No. of xpt .	$KMnO_4$ added.	$C_2O_4H_2$ added.	$KMnO_4$ for oxid.	TeO_2 taken.	TeO_2 found.	TeO_2.
	c c	c c.	c.c.	gram.	gram.	p c
62	36·65	16	20·65	0·1627	0·1648	101·3
63	14·47	21	23·47	0·1845	0·1873	101·5

absence of manganic sulphate, and it remained, therefore, to study further the cause of this phenomenon. It was, indeed, found that it is a function of the amount of sulphuric acid present in the solution.

In the following experiments, a weighed quantity of tellurium dioxide was dissolved in the smallest amount of sodium hydroxide, and measured volumes of this solution were mixed with successively increasing volumes of sulphuric acid of 42 per cent. (1 : 1). 1 c.c. of the acid was sufficient to bring the precipitated acid into solution. The following table contains only the volumes of decinormal permanganate used, the volume calculated from the equation VI necessary for oxidation without evolution of oxygen being taken as = 100.

First Series. Taken 0·1709 *gram* TeO_2.

No. of expt.	$KMnO_4$ for oxid.	Per cent.	H_2SO_4 1 : 1.
	c.c		c.c.
—	(21·42)	100·0	—
64	21·59	100·8	0·5
65	21·63	101·0	1·0
66	21·65	101·1	1·5
67	21·63	101·0	2·0
68	21·52	100·5	3·0
69	21·59	100·8	5·0
70	21·59	100·8	5·0
71	21·63	101·0	10·0
72	21·78	101·7	20·0

Second Series. Taken 0·1437 *gram* TeO_2.

No. of expt.	$KMnO_4$ for oxid.	Per cent.	H_2SO_4 (1 · 1)
	c.c.		c.c.
—	(18·01)	100·0	—
73	18·21	101·1	10
74	18·29	101·6	20
75	18·41	102·2	30
76	19·06	105·8	50
77	19·19	106·6	100
78	20·42	113·4	25*
79	21·13	122·9	50*

* Concentrated acid.

It will be seen from the above experiments that the evolution of free oxygen increases with the increase in the amount of sulphuric acid present, but the results are identical within experimental error, so long as the volume of sulphuric acid present does not exceed 10 c.c. It must be understood that dilution with water does not alter the amount of permanganate used—a fact confirmed by numerous experiments, an account of which is, however, omitted.

It is probable that the fact that more permanganate is used than is theoretically necessary, and the evolution of free oxygen connected with it, is due to the presence of sulphuric acid. This reaction is, therefore, a peculiarity of the nascent telluric acid, which causes part of the oxygen atoms from the permanganate to arrange themselves in diatomic and triatomic molecules.

With regard to the practical use of the process in estimating tellurium dioxide in a sulphuric acid solution by means of permanganate, it will be necessary, after subtracting the permanganate corresponding with the oxalic acid added, to multiply by the corrected coefficient 0·0078932 (log. = 7·89725), instead of by the theoretical coefficient 0·00798 gram, resulting from the equation VI. On using this factor in calculating the above series of Exps. 27 to 54, very satisfactory results are obtained, having due regard to unavoidable experimental errors. For the absolute error of the minimum experiment (35) amounts only to −0·0006 gram, and of the maximum experiment (52) to +0·0008 gram TeO_3. The application of the method is seen still better from the following experiments:—

No. of expt.	$KMnO_4$ added.	$C_2O_4H_2$ back.	$KMnO_4$ for oxid.	TeO_2 taken.	TeO_2 found.	Difference.
	c.c.	c.c.	c.c.	gram.	gram.	gram.
80	30·59	10	20·59	0·1627	0·1625	−0·0002
81	30·61	10	20·61	,,	0·1627	0·0000
82	31·57	11	20·57	,,	0 1623	−0·0004
83	34·34	11	23·34	0·1845	0·1842	−0·0003
84	33·40	10	23·40	,,	0·1847	+0·0002
85	36·55	13·1	23·45	,,	0·1851	+0·0006
86	34·37	11	23·37	,,	0·1845	0·0000
87	36·40	13	23·40	,,	0·1847	+0 0002

The calculation with the corrected coefficient gives theoretically the same result as if the permanganate had been standardised with weighed quantities of tellurium dioxide; practically, the result is better, as the coefficient depends on a mean number obtained from a large series of experiments.

Experiments in Alkaline Solution.

As, in estimating tellurous acid with permanganate in the presence of sulphuric acid, evolution of free oxygen takes place, I hoped to obtain better results by working in alkaline solution; under these conditions no evolution of oxygen takes place.

On adding potassium permanganate solution to one of tellurous acid in sodium hydroxide (containing sodium tellurite), a green coloration is momentarily produced (formation of manganate), but the liquid soon becomes brown, and manganese dioxide separates, according to the following equation:—

$$\text{X.}\quad 2KMnO_4 + 3TeO_2 = K_2O + 2MnO_2 + 3TeO_3.$$

In fact, an alkali tellurate is formed, and probably also some telluric compound of manganese.

The following experiment proves that the process strictly corresponds with the equation X.

Exp. 88.—0·18 gram TeO_2 requires, according to the equation V, 22·56 c.c. of decinormal permanganate for oxidation. 2 mols. of $KMnO_4$ oxidise in case VI, 5 mols., in case X, 3 mols., of TeO_2, so that the relation of volumes of permanganate necessary for oxidation of one and the same quantity of dioxide becomes VI : X = 3 : 5. In alkaline solution, the quantity of permanganate used for the oxidation of 0·18 gram of TeO_2 becomes, therefore, $22·56 \times \frac{5}{3} = 37·6$.

On carrying out the experiment, there was a distinct violet coloration, after the addition of from 37·6 to 38 c.c. of permanganate.

In practice, a decided excess of permanganate is run into a solution of tellurium dioxide in pure sodic hydrate, after which dilute sulphuric acid is added in some excess, and then, for the destruction of the higher compounds of manganese, decinormal oxalic acid, in quantity corresponding with about one-half of the volume of permanganate is added, after which the liquid, heated to 60°, is titrated back in the usual way with permanganate.

Several preliminary experiments show the applicability of the method.

No. of expt.	$KMnO_4$ added.	$C_2O_4H_2$ back.	$KMnO_4$ for oxid.	TeO_2 taken.	TeO_2 found.
	c.c.	c.c.	c.c.	gram.	gram.
89	42·59	20	22·59	0·1800	0·1803
90	42·58	20	22·58	”	0·1802
91	41·55	19	22·55	”	0·1800
92	41·55	19	22·55	”	0·1800
93	42·56	20	22·56	”	0·1800

In order to avoid errors due to the measuring of the test solutions, somewhat larger quantities of tellurium dioxide, dried at 105°, were weighed out, and dissolved in caustic soda separately for every experiment. While the permanganate was being run in, no evolution of oxygen took place, but on the addition of sulphuric acid, a feeble but distinct smell of ozone was observed. This requires that, as a mean, 0·35 per cent. of permanganate more is required for oxidation over and above the theoretical quantity calculated from VI. On using decinormal oxalic acid for standardising the permanganate, every c.c. of the decinormal solution is to be multiplied in this case by the corrected coefficient 0·007952 gram (log. = 7·90048).

In the following table (Exp. 94—102), in col. V, numbers are contained which give the permanganate used when the quantity calculated under the assumption that the reaction corresponds with the equation VI is taken = 100, and col. VII contains the numbers calculated with the corrected coefficient:—

No. of expt.	$KMnO_4$ added.	$C_2O_4H_2$ back.	$KMnO_4$ for oxid.	Per cent.	TeO_2 taken.	TeO_2 found.	Difference.
	c.c.	c.c.	c.c.		gram.	gram.	gram.
94	78·38	35	42·38	100·36	0·3370	0·3370	0·0000
95	68·17	33	35·17	100·47	0·2793	0·2797	+0·0004
96	131·90	60	71·90	100·39	0·5716	0·5718	+0·0002
97	99·75	43	56·75	100·31	0·4515	0·4513	−0·0002
98	179·04	78	101·04	100·45	0·8027	0·8035	+0·0008
99	61·68	27	34·86	100·44	0·2755	0·2758	+0·0003
100	75·69	33	42·70	100·24	0·3400	0·3396	−0·0004
101	114·52	50	61·52	100·31	0·5132	0·5137	+0·0005
102	133·89	61	72·89	100·20	0·5806	0·5796	−0·0010

Mean, 100·35.

The numbers contained in col. VII differ but very little from the quantities actually taken (col. VI, as a minimum by ± 0·0000 gram and as a maximum by + 0·0008 and — 0·0010), so that, if we consider that an error in measuring of ± 0·1 c.c. corresponds with an error of ± 0·0008 gram of TeO_2, the estimation of tellurium dioxide in alkaline solution, by means of permanganate, may be considered to be no less accurate than the estimation of ferrous oxide with the same reagent.

As regards the practical application of the method, the following may be remarked:—

If tellurium dioxide is to be determined in hydrochloric solution, either the stannous chloride method described in my first paper may be used for the approximate estimation, or, as a hydrochloric solution cannot be titrated with permanganate, the following process may be employed :—The hydrochloric solution is evaporated with a small quantity of sulphuric acid on the water bath until no more hydrochloric acid escapes, the last traces being driven off by heating the residue in a sand bath until fumes of sulphuric acid are evolved. There is no fear that tellurium tetrachloride will be volatilised, as tellurous sulphate is formed. To the residue, some water and sodium hydroxide are added until solution takes place, after which an estimation is made with permanganate in the manner described.

Exp. 103.—0·1765 gram of TeO_2 was dissolved in 5 c.c. strong hydrochloric acid and evaporated with 0·5 c.c. H_2SO_4. After solution in sodium hydroxide, 22·23 c.c. of decinormal permanganate was used for oxidation, which corresponds with 0·1768 gram of TeO_2 instead of the 0·1765 gram taken. This shows the accuracy of the method.

I append the analyses of several tellurium preparations.

Exp. 104.—An analysis was made of the product obtained on dissolving tellurium in aqua regia, and repeatedly evaporating to dryness with nitric acid; this was considered by Wills (this Journ., 1879, Trans., 70 *et seq.*) to be telluric hydrate. It contains in reality tellurous, telluric and nitric acids together with water, but the question was to estimate as dioxide the amount of tellurium present. This was done both (*a*) gravimetrically and (*b*) volumetrically.

(*a*.) 0·867 gram of the product dried at 105° gave, on heating to feeble redness, 0·745 gram of TeO_2.

(*b*.) 0·3455 gram of substance was dissolved in hydrochloric acid and evaporated with H_2SO_4.

The acid solution required 37·57 c.c. decinormal permanganate = 0·29655 gram of TeO_2,

	(*a*.) Gravimetrically.	(*b*.) Volumetrically.
Percentage of TeO_2....	85·93	85·83

Exp. 105.—Analysis of basic tellurous sulphate. 0·243 gram in sulphuric solution, required 24·67 c.c. of the permanganate solution = 0·1947 gram of TeO_2 = 80·1 per cent. Calculated for Te_2O_4,SO_3 = 80·0 per cent.

Exp. 106.—Analysis of tellurium tetrabromide. 2·6242 grams of the pure tetrabromide used for the atomic weight determinations was heated with a large excess of sulphuric acid on the water bath, but even after a week's action, both in concentrated and dilute solution, only a slight decomposition took place. In order to expel the bromine, the solution was cautiously heated with an excess of nitric acid, which acts very violently, and the excess of acid was then removed by evaporation until fumes of sulphuric acid appeared. From the solution diluted to 150 c.c., 20 c.c. representing 0·3499 gram of

$TeBr_4$ required as a mean 15·8 c.c. of the permanganate for oxidation = 0 0997 gram of Te (coefficient 1 c.c. = 0·00063106 gram Te). Percentage of Te : found : 28·50 ; calculated 28·52 (for $TeBr_4$).

I venture to think that the volumetric estimation of tellurium by means of permanganate is more exact than any other method for its determination, and at the same time the results are obtained in much less time. The volumetric estimation of telluric acid will form the object of a future paper.

XXIX.—*Fermentations induced by the Pneumococcus of Friedländer.*

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AMONGST the numerous contributions which have been made by Brieger to our knowledge of the chemical products resulting from the vital processes of micro-organisms, there are two (*Zeit. physiol. Chem.*, 8, 306—31, and 9, 1—7) on the substances formed in the cultivation of the well known *Pneumococcus* of Friedländer in certain media.

By growing this specific micro-organism in suitable solutions of grape or cane sugar, Brieger obtained principally acetic acid, together with some formic acid and ethyl alcohol. The same products were also obtained by the growth of this organism in solutions of calcium lactate and creatine. As these transformations are only incidentally described by Brieger, without the precise relative proportions of the products having been determined, we have endeavoured to place these fermentations on a more quantitative basis, and to further investigate the behaviour of this micro-organism towards other carbohydrates.

In our experiments, the *Pneumococcus* employed was originally obtained by one of us from the Hygienic Institute of Berlin, in January, 1886, and continuously further cultivated for a period of nearly three years on gelatin-peptone before being used for fermentation purposes.

In order to ensure the purity of the organism used in the following experiments, we submitted one of the growths to plate-cultivation, and thus made a single colony the basis of further operations.

It is unnecessary to enter into a description of the morphological characters of the *Pneumococcus* (Friedländer) which is to be found in any of the modern text-books of bacteriology.

Fermentation of Glucose.

The following solution was prepared for the purpose:—

Glucose, 60 grams.................	the whole made up with distilled water to 2000 c c.
Peptone, 6 grams..................	
Liebig's *extract. carnis*, 2 grams.....	
Calcium carbonate, 20 grams.......	

This solution was placed in a capacious flask, plugged with sterile cotton-wool, and the whole was then finally sterilised by steaming for two hours on each of three successive days.

The sterile solution was inoculated with a single loop of a platinum needle, which had been dipped into a culture derived from one of the colonies referred to above, the flask being then placed in the incubator at 39° C. On the following day the liquid was already in active fermentation, which, however, only continued for a period of two days, and as by the sixth day all visible action had ceased, the liquid was forthwith submitted to analysis.

Two-thirds of the liquid were, in the first place, distilled off, and the distillate worked up for alcohols. To this end it was redistilled several times, two-thirds of the liquid only being taken over on each occasion. When the liquid had in this manner been reduced to about 1000 grams, its density was carefully taken by means of the specific gravity bottle. In this way 64·6876 grams of liquid, sp. gr. 0·9983 (at 15·5°), were obtained, corresponding to 0·91 per cent., or 0·5897 gram ethyl alcohol.

As a check on this determination, the liquid was again repeatedly distilled, until only about one-half of the former volume remained. On then again taking the density, the 33·4826 grams of liquid were found to have a sp. gr. of 0·99757, corresponding to 1·34 per cent., or 0·4487 gram ethyl alcohol.

The residue from which the alcohol had been distilled in the first instance, and which would contain any acids in the condition of calcium salts, was treated with 340 c.c. of normal hydrochloric acid (the quantity required to neutralise the 20 grams of calcium carbonate used was 348·3 c.c.), an insufficient quantity of acid being added in order to only partially liberate the organic acids, and thus obtain a purer product on distillation.

The liquid thus partially neutralised with hydrochloric acid was distilled down to a small bulk, and the distillate boiled up with excess of barium carbonate (see Frankland and Fox, "On a Pure Fermentation of Mannite and Glycerin," *Proc. Roy. Soc.*, **46**, 345—357). In this manner, 1·5422 gram barium salt, dried at 130°, was obtained, yielding on ignition with sulphuric acid, 90·73 per cent. barium sulphate. Barium acetate yields 91·37 per cent. barium sulphate.

The above salt must, therefore, have been almost pure barium acetate, possibly mixed with a trace of a salt of a fatty acid of higher molecular weight.

To the residue in the distilling flask, water was added, and the distillation again carried to small bulk; from the distillate, 1·4434 gram of barium salt was similarly obtained, yielding 94·72 per cent. of barium sulphate. This second salt must, therefore, have been a mixture of barium acetate and formate, thus:—

Barium formate yields 102·64 per cent. barium sulphate.

In fact, the percentage 94·72 barium sulphate corresponds to—

1·0144 gram of barium acetate.
0·4290 „ „ formate.

The full quantity of hydrochloric acid was now added to the residue in the distilling flask, and the two further distillates obtained were united and converted into 0·3752 gram of barium salt, yielding 92·06 per cent. of barium sulphate, thus corresponding to—

0·3522 gram of barium acetate.
0·0230 „ „ formate.

Six more distillates were obtained giving together only 0·1620 gram of barium salt, yielding 90·99 per cent. of barium sulphate, and thus consisting of almost pure barium acetate.

The residue left after distilling off the volatile acids as above was repeatedly shaken out with ether, and the united ethereal extract, after driving off the ether, was treated with excess of carbonate of soda. The sodium salt thus obtained was extracted with absolute alcohol, and the insoluble residue, after being dissolved in water, was acidified with hydrochloric acid, and repeatedly shaken out with ether. The ethereal extract yielded, on evaporation, a residue weighing 0·0280 gram, which was presumably succinic acid, as it gave the characteristic irritating fumes of the latter on ignition.

The products of the fermentation in question may be thus summarised:—

Ethyl alcohol..	0·5897 gram.	
Acetic acid....	1·4451 „	(Barium acetate = 3·0708 gram).
Formic acid ..	0·1832 „	(Barium formate = 0·4520 „).
Succinic acid..	0·0280 „	

Fermentation of Mannitol. I.

The following solution of mannitol

Mannitol	60 grams	the whole made up with distilled water to 2000 c.c.
Peptone	2 „	
Carbonate of lime	15 „	
Salt solution	200 c.c.	

was prepared, and, after due sterilisation, was inoculated with a single loopfull of a pure cultivation of the pneumococcus in a similar mannitol solution. After inoculation the mannitol solution was placed in the incubator at 39°, and remained there 40 days, until the slow fermentation which set in had entirely ceased. The liquid was then submitted to a perfectly similar process of analysis to that above described for the glucose fermentation. The volatile acids yielded the following barium salts :—

I. 5·0513 grams of barium salt (dried at 130°), yielding 4·6161 grams $BaSO_4$ = 91·38 per cent. $BaSO_4$ (barium acetate yields 91·37 per cent. $BaSO_4$).

II. 1·2320 gram barium salt, yielding 1·0976 gram $BaSO_4$ = 89·09 per cent. $BaSO_4$.

III. 0·0750 gram barium salt, yielding 0·0628 gram $BaSO_4$ = 83·74 per cent. $BaSO_4$.

Thus, as in the case of the glucose fermentation, the volatile acids consisted chiefly of acetic acid, but traces of formic acid were also detected qualitatively, and the salts II and III, from the percentage of barium sulphate which they yielded, appeared to contain some higher fatty acid, but owing to the small total quantity of salt, the nature of this acid could not be further investigated.

The distillate from the fermented liquid, after repeated rectification, yielded 64·0874 grams of liquid of sp. gr. (at 15·5°) 0·9890, corresponding to 6·42 per cent. of ethyl alcohol by weight or 4·11 grams of ethyl alcohol. On further concentrating the liquid by repeated rectification, 31·7790 grams of liquid of 0·9809 sp. gr. were obtained, corresponding to 12·46 per cent. or 3·96 grams of ethyl alcohol. The liquid was dried with anhydrous potassium carbonate, after which its boiling point was found to be 79°.

From the residue, after distilling off the volatile acids as described above, a minute quantity (0·0108 gram) of succinic acid was obtained.

Fermentation of Mannitol. II.

A second experiment on mannitol was made in order to ascertain whether the fermentation would be more complete if a larger quantity of nitrogenous nutriment were provided for the organism. For this purpose the following solution was prepared:—

Mannitol	60 grams	the whole made up with distilled water to 2000 c.c.
Liebig's *extract. carnis* ...	2 ,,	
Peptone	6 ,,	
Carbonate of lime	20 ,,	

This solution, after sterilisation, was inoculated as before from a mannitol cultivation of the pneumococcus, and submitted to analysis after remaining 36 days in the incubator at 39°.

The following products were obtained:—

Volatile Acids.

I. 4·1798 grams barium salt (dried at 130°), yielding 3·8154 grams $BaSO_4$ = 91·28 per cent. $BaSO_4$ (barium acetate yields 91·37 per cent. $BaSO_4$).

II. 1·3784 gram barium salt, yielding 1·2498 gram $BaSO_4$ = 90·67 per cent. $BaSO_4$.

III. 1·1604 gram barium salt, yielding 0·9808 gram $BaSO_4$ = 84·52 per cent. $BaSO_4$ (barium propionate yields 82·32 per cent. $BaSO_4$).

Thus again whilst the principal volatile acid is acetic there is evidence of a considerable proportion of a higher fatty acid, probably propionic. The last fractions of salts obtained as above are, however, always gummy in appearance, and the low percentage of barium may, therefore, not impossibly be due to some other impurity and not to a higher fatty acid; this applies also to the last fractions of barium salt obtained in the previous fermentation (see p. 255).

Alcohols.—After repeated rectification, 63·9424 grams of liquid of sp. gr. 0·9868, corresponding to 7·92 per cent. of alcohol, or 5·06 grams, were obtained. This liquid, after further repeated rectification, yielded 31·6842 grams of sp. gr. 0·9779, corresponding to 14·83 per cent. of alcohol, or 4·70 grams. On drying the alcohol with anhydrous potassium carbonate, its boiling point was found to be 79°, or that of ethyl alcohol.

Fixed Acid.—A trace of what was apparently succinic acid was extracted from the residue after distilling off the volatile acids.

The products of the three fermentations examined may be thus summarised:—

	I. Glucose, with peptone and extract of meat.	II. Mannitol, with peptone only.	III. Mannitol, with peptone and extract of meat.
Ethyl alcohol	0·5897 grm.	4·11 grms.	4·06 grms.
Volatile acids calculated as acetic acid	1·6578 ,,	2·9921 ,,	3·1617 ,,

The above results show that in each case, and especially in that of the glucose, only a very partial decomposition had taken place, moreover neither the extent nor the nature of this fermentative decomposition was materially altered in the more nutritious medium produced by the addition of extract of meat and a larger quantity of peptone.

The products of the fermentation, essentially ethyl alcohol and acetic acid, are similar to those obtained by one of us (*loc. cit.*) in the fermentation of mannitol by a totally different organism, the *Bacillus ethaceticus*. Indeed, not only are the products of fermentation similar in their nature, but the proportion in which they are respectively formed is almost identical in the two cases; thus—

	Mannitol fermented by *Pneumococcus*	
	I.	II.
Proportion of alcohol to volatile acids, calculated as acetic acid.	1·37	1·60
	Mannitol fermented by *Bacillus ethaceticus*.	
	I.	II.
	1·63	1·63

This ratio corresponds closely to the molecular proportions:—

$$\begin{array}{ccc} 2C_2H_5\cdot OH & : & CH_3\cdot COOH = 1\cdot 53. \\ (2 \times 46) & & (60) \end{array}$$

But although the alcohol and acetic acid, produced in the fermentations in question, thus stand to each other in virtually the same proportion, the absolute amounts produced are much less in the case of the *Pneumococcus* than in that of the *B. ethaceticus* fermentation. In fact, in the most complete of the latter fermentations practically twice the amount of these products was obtained, as with the *Pneumococcus*, thus:—

Mannitol Fermentations.

	Bacillus ethaceticus.	*Pneumococcus.*
Alcohol	11·415 grams.	5·06 grams.
Acetic acid	7·008 „	3·16 „

It is very noticeable that mannitol, as the above results show, is more readily fermentable by the *Pneumococcus* than glucose; this point we have not only confirmed qualitatively several times, but we have also compared the relative facility with which the several substances which we have found to be attacked by this organism are fermented.

Thus on inoculating from one and the same cultivation* of the *Pneumococcus* into similar solutions† of glucose, mannitol, cane-sugar, and dextrin, and preserving all at 39°, the

Glucose fermented on the 6th day after inoculation.
Mannitol „ „ 5th „ „
Cane-sugar „ „ 5th „ „
Dextrin „ „ 5th „ „

Again on inoculating from the latter mannitol culture (when it was 13 days old) into similar solutions, the

Glucose fermented on the 4th or 5th day after inoculation.
Mannitol „ „ 3rd day after inoculation.
Cane-sugar „ „ 3rd „ „
Dextrin „ „ 3rd „ „

Whilst on inoculating from the latter mannitol culture (when it was nine days old), the glucose, mannitol, and cane-sugar all commenced fermenting on the same day, viz., the third after inoculation. (No dextrin solution was inoculated in this case.)

Again, on inoculating from a glucose broth‡ culture (five days old), the

Glucose fermented on the 4th or 5th day after inoculation.
Mannitol „ „ 3rd day after inoculation.
Cane-sugar „ „ 2nd „ „
Dextrin „ „ 4th or 5th day after inoculation.

Similarly on inoculating from an ordinary gelatin culture, the

Glucose fermented on the 8th day after inoculation.
Mannitol „ „ 4th „ „
Cane-sugar „ „ 4th „ „

In this case the glucose fermentation was also visibly feebler than the other two.

Thus, although there is some irregularity§ in the several series of experiments as to the precise period which elapses between the time of inoculation and the commencement of fermentation, the balance of evidence points to the glucose being the least, and to the mannitol and cane-sugar being the most readily fermentable.

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* This culture was in a 3 per cent. solution of mannitol, as given on page 255; it was 6 days old at the time.

† These were all 3 per cent. solutions, similar to the mannitol.

‡ A 3 per cent. solution of glucose in water to which one-tenth of its volume of the ordinary peptone broth has been added.

§ This irregularity doubtless depends upon the quantity of ferment inoculated, and also upon differences in its vitality at the time of inoculation.

We have repeatedly endeavoured to ferment dulcitol with the *Pneumococcus*, but have invariably failed. The *Pneumococcus*, therefore, like the *B. ethaceticus*, possesses the extremely interesting property of discriminating between the isomeric bodies mannitol and dulcitol.

Unlike the *B. ethaceticus*, the *Pneumococcus* does not ferment glycerol.

The Fermentation Gases.

The decompositions of glucose and mannitol recorded above are attended with a considerable evolution of gas, the nature of which has been further investigated by one of us. For this purpose, small, narrow-mouthed bottles of a little more than 100 c.c. capacity were employed; 100 c.c. of solutions of glucose and mannitol respectively were introduced into these, which were then plugged with sterile cotton wool, and the whole steam-sterilised on three successive days. These bottles were then inoculated from a fermenting cultivation of the *Pneumococcus*, and the cotton-wool stoppers rapidly exchanged for indiarubber ones fitted with delivery tubes, both of which had been duly sterilised with steam, each delivery tube also contained a small plug of asbestos to prevent the passage of unsterilised air into the bottle.

The inoculated bottles so fitted were then placed in an incubator, kept at about 36°, whilst the delivery-tubes passed through apertures cut in the side of the latter, and dipped into a mercury-bath. The evolved gases were then collected in a series of test-tubes, roughly measured, and several samples representative of the various stages of the fermentation were submitted to careful quantitative analysis.

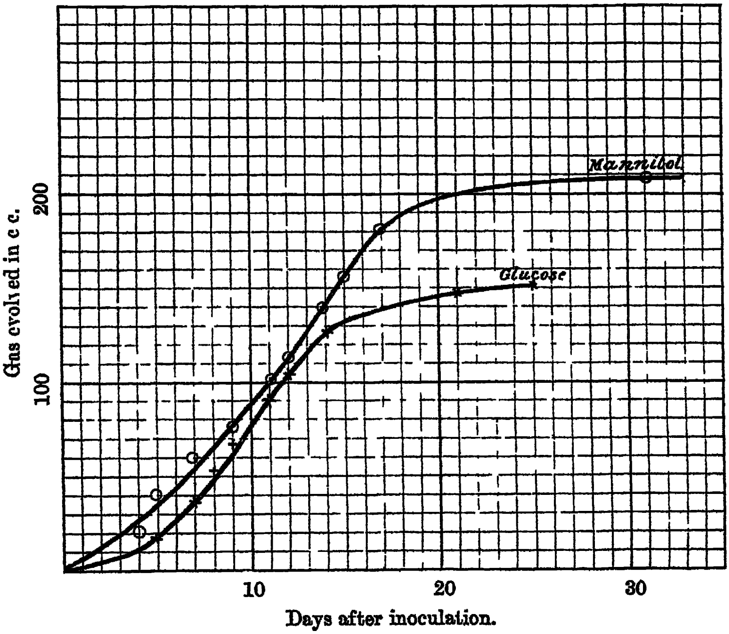
In the following table (p. 261), the volumes of gas collected during the two fermentations are recorded.

Thus the total volume of gas collected in the fermentation of the 3 grams of glucose was 150·5 c.c., and in that of the same quantity of mannitol 209·6 c.c. As the measurements were only approximative, it has not been considered worth while to correct them for temperature and pressure (the temperature was in all cases about 16—18°). It will be seen that the volumes of gas given off in the two cases fully confirms what has been stated above concerning the more ready fermentation of the mannitol.

The progress of the fermentations is more readily followed by means of the following graphic representation, in which the abscissæ represent the lapse of time in days since inoculation, whilst the

No. of days after inoculation.	Glucose.		Mannitol.	
	Volume of gas.	Total volume of gas collected.	Volume of gas.	Total volume of gas collected.
4	—	—	Tube (1) 21·6 c c.	21·6 c.c.
5	Tube (1) 16·3 c.c.	16·3 c.c.	„ (2) 18·3 „	39·9 „
7	„ (2) 21·3 „	37 6 „	„ (3) 20·6 „	60·5 „
8	„ (3) 16·2 „	53·8 „	—	—
9	„ (4) 11 4 „	65·2 „	„ (4) 16·8 „	77·3 „
11	„ *(5) 24·0 „	89·2 „	„ *(5) 23·5 „	100·8 ,
12	„ (6) 18·1 „	1 07·3 „	„ (6) 12·7 „	113·5 „
14	„ (7) 20·6 „	127·9 „	„ (7) 27·1 „	140·6 „
15	—	—	„ (8) 14·7 „	155·3 „
17	—	—	„ *(9) 27·1 „	182·4 „
21	„ *(8) 19·0 „	146·9 „	—	—
25	„ (9) 3·6 „	150·5 „	—	—
31	—	—	„*(10) 24·5 „	206·9 „
—	—	—	2 7 „	209·6 „

ordinates denote the volume of gas given off, measured in cubic centimetres.



In order to ascertain the composition of the fermentation gases, samples of the gas evolved at different stages of the fermentation were submitted to careful analysis. The portions of the evolved gas submitted to analysis are indicated in the above table by a *.

Thus in the case of the glucose fermentation, the 5th and 8th tubes, and, in the case of the mannitol fermentation, the 5th, 9th, and 10th tubes of gas were analysed.

The following are the results of analysis stated in parts per 100 by volume.

Glucose Fermentation.

	Tube 5.			Tube 8.		
	I.	II.	Mean.	I.	II.	Mean.
CO_2	51·06	51·22	51·14	56·62	56·51	56·57
O	0·09	0·05	0·07	0·00	—	0·00
H	47·26	47·55	47·41	43·20	43·29	43·24
N	1·59	1·18	1·38	0·18	0·20	0·19
	100·00	100·00	100·00	100·00	100·00	100·00

Proportion of H : CO_2 = 1 : 1·08. Proportion of H : CO_2 = 1 : 1·31.

Mannitol Fermentation.

	Tube 5.			
	I.	II.	III.	Mean.
CO_2	51·80	51·56	51·45	51·60
O	0·19	0·22	0·00	0·14
H	47·07	47·64	47·88	47·53
N	0·94	0·58	0·67	0·73
	100·00	100·00	100·00	100·00

Proportion of H : CO_2 = 1 : 1·09.

Mannitol Fermentation.

	Tube 9.			Tube 10.*		
	I.	II.	Mean.	I.	II.	Mean.
CO_2 ……	54·68	54·65	54·67	50·57	50·57	50·57
O ……..	0·06	0·17	0·11	1·70	1·68	1·69
H ……..	45·21	45·18	45·20	42·45	42·44	42·44
N ……..	0·05	0·00	0·02	5·28	5·31	5·30
	100·00	100·00	100·00	100·00	100·00	100·00

Proportion of H : CO_2 = 1 : 1·21. Proportion of H : CO_2 = 1 : 1·19.

The fermentation-gases consist thus exclusively of carbonic anhydride and hydrogen, and in no case was there any trace of methane or other gas yielding carbonic anhydride on explosion with oxygen. The small quantity of nitrogen found in the early tubes in each case is due to the residual air in the fermentation-bottles and delivery-tubes, which contained, of course, a few cubic centimetres of air above the liquid. The analyses, moreover, show that a part of the oxygen of this air had been absorbed by the fermenting liquid, or rather by the organism, which is capable of both aërobic and anaërobic life and activity.

With the exception of the ordinary butyric fermentation, this is, as far as we are aware, the only pure fermentation in which the evolution of hydrogen has been demonstrated. The same gas, as will afterwards be shown, is also evolved in the fermentations excited by the *B. ethaceticus*, which have been described by one of us.

The proportion of hydrogen to carbonic anhydride by volume shows that these gases are given off in approximately the same number of molecules of each, or, more accurately, 10 mols. of hydrogen to 13 mols. of carbonic anhydride in the case of the glucose, and 10 mols. of hydrogen to 12 mols. of carbonic anhydride in that of the mannitol. This larger proportional evolution of hydrogen in the case of the mannitol is what might have been anticipated from a consideration of the larger percentage of hydrogen in mannitol than in glucose.

The carbonic anhydride evolved, it must also be borne in mind, is not wholly obtained from the primary decomposition of the glucose or mannitol, but is also partially a secondary product derived from the decomposition of the carbonate of lime by the acetic and formic acids to which the fermentation gives rise.

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* A bubble of air accidentally gained access to this tube in removing it from the mercury-bath; hence the high percentages of oxygen and nitrogen found.

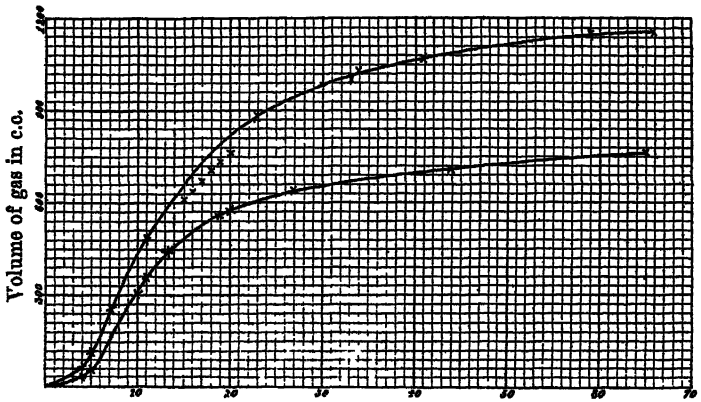
In order to further examine the evolved gases, and determine, not only the ratio between the carbonic anhydride and hydrogen, but also between these and the amounts of alcohol, acetic and formic acids produced, the experiments with the mannitol were repeated on a larger scale (using 400 c.c. of the 3 per cent. solution of mannitol). As we thought that possibly some of the gases might have diffused through the indiarubber stoppers of the fermenting bottles, we took the further precaution of thickly coating the outside of the stoppers with paraffin, thus rendering all diffusion or loss of gas out of the question.

The experiment was performed in duplicate, and the follow quantities of gas were obtained :—

Volume of Gas evolved in the Fermentation of 400 c.c. of Mannitol Solution (3 per cent.).

No. of days after inoculation.	Vol. of gas from Bottle I.	Total vol. of gas collected from Bottle I.	Vol. of gas from Bottle II.	Total vol. of gas collected from Bottle II.
4	64·7	64·7	34·4	34·4
5	35·8*	100·5	15·6*	50·0
7	156·8	257·3	—	—
10	—	—	260·0	310·0
11	224·0	481·3	50·6*	360·6
13	—	—	78·0	438·6
15	120·0	601·3	—	—
16	32·2*	633·5	—	—
17	31·2	664·7	—	—
18	36·0	700·7	—	—
19	40·3	741·0	117·4	556·0
20	26·0	767·0	15·8*	571·8
23	120·0*	887·0	—	—
27	—	—	63·2	635·0
33	126·0	1013·0	—	—
34	17·0*	1030·0	—	—
41	43·0*	1073·0	—	—
44	—	—	82·5	717·5
59	74·0	1147·0	—	—
66	6·8	1153·8	36·0	753·5

The evolution of gas can be more easily followed by reference to the graphic representation on p. 265, in which the ordinates represent the volumes of gas, and the abscissæ the time of fermentation.



Days after inoculation.

Mr. McCowan, B.Sc., Lecturer on Mathematics and Physics in University College, Dundee, has very kindly investigated the nature of these curves, and calculated their equations. He finds that although, as the above figure indicates, they are quantitatively different, yet qualitatively they are very much alike, and can be represented by similar equations. In both cases the initial portion of the curve with the upward concavity has been neglected, as this does not really reflect the progress of the fermentation, owing to the absorption of carbonic anhydride by the liquid in the first instance. It is only after about the 8th day that the curves assume their normal form.

The upper curve, representing the fermentation in which most gas was evolved, is defined by the equation

$$v = \frac{6{\cdot}73t^2}{1 - 0{\cdot}006t + 0{\cdot}00574t^2},$$

in which v = volume, in cubic centimetres, of gas evolved and t = time in days during which the fermentation has been proceeding.

Thus comparing the actually observed results with those obtained by calculation from the above equation, we have—

Days.	Volume (calculated).	Volume (observed).
5	151 c.c.	110 c.c.
10	444 ,,	435 ,,
20	847 ,,	825 ,,
30	1012 ,,	987 ,,
40	1083 ,,	1060 ,,
60	1137 ,,	1145 ,,

Thus from the 10th day to the close of the fermentation, the calculated and observed volumes exhibit the most striking concordance.

Again the lower curve, representing the fermentation in which the smaller volume of gas was evolved, is defined by the following equation:—

$$v = \frac{4{\cdot}96t^2}{1 - 0{\cdot}004t + 0{\cdot}0064t^2},$$

in which v and t have the same significance as above.

Thus comparing the calculated with the experimental results we find

Days.	Volume (calculated).	Volume (observed).
4	73·0 c.c.	34 c.c.
6	148·0 „	90 „
7	188·5 „	140 „
8	230·0 „	210 „
9	271·0 „	270 „
10	310·5 „	310 „
15	468·0 „	480 „
19	553·5 „	555 „
20	569·0 „	571 „
30	672·0 „	657 „
60	750·0 „	750 „

Here again, after the 8th day, the coincidence between experiment and calculation becomes very complete.

We believe that the irregularities in the results obtained in such fermentation experiments are due in the first instance to differences in the quantity and vitality of the organisms introduced, and secondly to the pressure under which the fermentations take place being subject to variations. Thus, in the above experiments, the evolved gases were collected over mercury, and the pressure in the fermenting bottles would obviously alter with the considerable variations in the depth of mercury in the trough, and it is more than possible, indeed from our knowledge of the action of carbonic anhydride under pressure, it is highly probable, that any increase of pressure would have the effect of checking the fermentation to an appreciable extent.

We are at present extending our observations on the evolution of gas during fermentation, and we shall in the future introduce precautions to guard against the probability of such irregularities arising.

Specimens of the gas given off at different stages of the two fermentations were again submitted to careful analysis, and in the preceding table the portions thus examined are indicated by a *.

The following results were obtained:—

Fermentation I.

	Composition of gases evolved on				
	5th day.	16th day.	23rd day.	34th day.	41st day.
CO_2	27·04	51·77	61·29	66·18	65·47
O	2·05	0·09	0·15	0·22	0·09
H	48·69	47·97	38·26	33·47	34·19
N	22·22	0·17	0·30	0·13	0·25
	100·00	100·00	100·00	100·00	100·00

Fermentation II.

	Composition of gases evolved on		
	5th day.	11th day.	20th day.
CO_2	19·86	50·07	58·45
O	3·55	0·07	0·21
H	36·74	49·52	41·30
N	39·85	0·34	0·04
	100·00	100·00	100·00

These analyses fully confirm the results obtained in the previous series of experiments made on the smaller scale. They show that the oxygen of the air present in the first instance in the fermenting bottle is rapidly consumed during the growth, and that the gas evolved is first richer in hydrogen than carbonic anhydride, which relationship is reversed in the latter part of the fermentations. This reversal is doubtless due to the carbonic anhydride being at first largely absorbed by the water of the fermenting liquid with formation of calcium bicarbonate, so that the real relationship between the carbonic anhydride and hydrogen evolved can only become apparent in the latter part of the fermentation, whilst at the very end the carbonic anhydride again predominates in consequence of the slow decomposition of the calcium bicarbonate at first formed. In round numbers *this relationship may be taken as* 6 *vols. or molecules of carbonic anhydride to* 4 *vols. or molecules of hydrogen*

After the completion of these fermentations we also determined the quantity of the other products, alcohol and volatile acids, according to the methods previously described.* We obtained the following results:—

	Fermentation I.	Fermentation II.
Alcohol—		
Barium salts	3·0615 grams.	2·321 grams.
Yielding $BaSO_4$..............	91·39 per cent.	90·89 per cent.
Equivalent to ethyl alcohol	1·106 gram.	0·837 gram.
Volatile acids—		
Barium salts..................	1·3055 gram.	1·467 gram.
Yielding $BaSO_4$	97·17 per cent.	96·29 per cent.
Equivalent to acetic acid	0·653 gram.	0·7276 gram.

On comparing these results with those obtained in the fermentations of mannitol on the larger scale, as recorded on p. 257, it will be seen that in the case of the small fermentations the quantities of alcohol and acetic acid obtained are approximately in the same proportion as those of the large fermentations. In the large fermentations 2000 c.c. of a 3 per cent. solution of mannitol were employed, in the small ones, on the other hand, only 400 c.c. of a similar solution; on multiplying the products obtained in the latter by five, we obtain the following comparative figures:—

	Large fermentations.		Small fermentations.	
	I.	II.	I*a*.	II*a*.
Alcohol	4·11 grams.	5·06 grams.	5·53 grams.	4·185 grams.
Volatile acids, calculated as acetic acid........................	2·9921 „	3·1617 „	3·265 „	3·6380 „
Proportion of alcohol to volatile acids, calculated as acetic acid..	1·37	1·60	1·69	1·15

The comparative uniformity of the decompositions brought about by this organism is the more noteworthy, when it is mentioned that the fermentations I and II took place in London in 1888, whilst I*a* and II*a* were carried out in Dundee in 1890, exactly two years later.

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* The mode of procedure was only altered in respect to the determination of the alcohol, which was effected by oxidation with chromic acid (see Frankland and Frew, this vol., p. 83).

Owing to the close agreement between the results of the fermentations II and I*a*, we shall take these as representing the typical course of the fermentative process and in the following deductions make use of these results only; the evolution of gas in the case of Fermentation I*a* being considerably in excess of that in Fermentation II*a*, also points to the former being the more complete of the two fermentations.

In the case of Fermentation I*a*, we have then the following quantities of the several products:—

Alcohol.	Acetic acid.	Carbonic anhydride.	Hydrogen.
1·106 gram.	0·653 gram.	1·3648 gram.	0·0413 gram.

In the calculation of the weights of the carbonic anhydride and hydrogen evolved, we have assumed that the average composition of the 1154 c.c. of evolved gas was 6 vols. of CO_2 to 4 vols. of H, as indicated by the analyses of the later portions of gas given off.

The above weights are found to stand in the following proportion:—

Alcohol.		Acetic acid.		Carbonic anhydride.		Hydrogen.
26·78	:	15·81	:	33·05	:	1

Now these figures are in very close accord with those corresponding to the following molecular proportions:—

$$\begin{array}{ccccccc} 9C_2H_6O & : & 4C_2H_4O_2 & : & 12CO_2 & : & 8H_2 \\ (9 \times 46) & & (4 \times 60) & & (12 \times 44) & & (8 \times 2) \\ 414 & & 240 & & 528 & & 16 \\ 25{\cdot}9 & : & 15{\cdot}0 & : & 33{\cdot}0 & : & 1 \end{array}$$

These products, alcohol, acetic acid, carbonic anhydride, and hydrogen, in the above proportions, are most readily referable to the decomposition of the mannitol according to the following equation:—

$$6C_6H_{14}O_6 + OH_2 = 9C_2H_6O + 4C_2H_4O_2 + 10CO_2 + 8H_2;$$

but the 4 molecules of acetic acid acting upon the excess of calcium carbonate employed in the fermentation will yield two further molecules of carbonic anhydride, thus

$$4C_2H_4O_2 + 2CaCO_3 = 2CO_2 + 2OH_2 + 2Ca(C_2H_3O_2)_2,$$

the net products determined being thus

$$9C_2H_6O + 4C_2H_4O_2 + 12CO_2 + 8H_2,$$

as calculated above from the results of actual experiment.

The results of our investigation may be summarised as follows:—

1.—The *Pneumococcus* of Friedländer sets up a fermentative process in suitable solutions of dextrose, cane-sugar, milk-sugar, maltose, raffinose. dextrin, and mannitol.

2.—It does not ferment solutions of dulcitol or glycerol, and has thus the power, like the *Bacillus ethaceticus*, of distinguishing between the isomers mannitol and dulcitol.

3.—In the fermentation of dextrose and mannitol, the principal products are ethyl alcohol and acetic acid with a smaller proportion of formic acid and traces of a fixed acid, in all probability succinic acid.

4.—The gaseous products are carbonic anhydride and hydrogen.

5.—The ethyl alcohol, volatile acids (calculated as acetic acid), carbonic anhydride, and hydrogen approximate to the molecular proportions

$$9C_2H_6O, 4C_2H_4O_2, 12CO_2, 8H_2.$$

6.—The production of which may be most readily referred to the following equations:—

$$6C_6H_{14}O_6 + OH_2 = 9C_2H_6O + 4C_2H_4O_2 + 10CO_2 + 8H_2,$$

which is followed by

$$4C_2H_4O_2 + 2CaCO_3 = 2CO_2 + 2OH_2 + 2Ca(C_2H_3O_2)_2$$

A CORRECTION

Action of Heat on Nitrosyl Chloride.

By J. J. SUDBOROUGH and J. H. MILLAR.

In our paper on the action of heat on nitrosyl chloride, published in the February number of the Transactions (this vol., p. 73), we gave the percentage of dissociation corresponding to each density determined experimentally. We are indebted to Mr. Norman Leonard, B.Sc., for pointing out that, owing to an erroneous assumption, the figures given in the last column in the table, p. 80, are too high. The corrected percentages of dissociation should stand as follows :—

Temperature.	
784°	5·54
796	8·22
815	10·64
928	25·17
968	39·19
985	41·85

XXX.—*Contributions to our Knowledge of the Aconite Alkaloids. Part I. On the Crystalline Alkaloid of* Aconitum napellus.

By Professor W. R. DUNSTAN and W. H. INCE, Ph.D.

(From the Research Laboratory of the Pharmaceutical Society.)

THE discovery of an alkaloïd in the root of *Aconitum napellus* was made by Geiger and Hesse (*Annalen*, 7, 276) in the year 1833. This alkaloid, which they did not succeed in crystallising, was named "aconitine." Some years later, von Planta (*Annalen*, 74, 257) obtained what was apparently the same alkaloïd and analysed it in the amorphous state. The analytical data pointed to the formula, $C_{30}H_{47}NO_7$.

In 1860, T. B. Groves (*Pharm. Journ. Trans.* [2] viii, 121) obtained from the root of this plant a crystalline alkaloïd which furnished crystalline salts. In 1871, Duquesnel (*Ann. Chim. Phys.* [4], 25, 151) pointed out that the method of Geiger and Hesse which was generally employed in extracting the alkaloid from the root was objectionable, since it involved heating the substance with mineral acids and with alkalis, both of which were likely to decompose it. Duquesnel believed that the amorphous character of commercial specimens of the alkaloïd was due to the presence of decomposition products of the crystalline alkaloïd formed during its extraction. The process suggested by him for obtaining the alkaloïd from the root was intended to obviate these defects. The powdered root is exhausted with alcohol acidified with tartaric acid, an acid which, unlike mineral acids, does not attack the alkaloïd. The alcoholic solution is concentrated at a low temperature (60°), and then precipitated with sodium hydrogen carbonate. The precipitate is crystallised from a mixture of ether and light petroleum.

The alkaloïd thus obtained, melted at 140°, and on combustion yielded numbers which agreed best with the formula $C_{27}H_{40}NO_{10}$. It was lævorotatory and furnished crystalline salts.

In 1875, the question as to the nature of the aconite alkaloïds was taken up by Dr. C. R. A. Wright, whose researches were aided by grants from the British Pharmaceutical Conference. This enquiry lasted many years, and was productive of a number of interesting and important results which may be briefly summarised here, so far as they relate to the alkaloïds of *Aconitum napellus.*

The crystalline nitrate prepared by Mr. T. B. Groves was chemically examined. The base regenerated from this salt afforded, on combustion, numbers which stand about midway between those calculated from the formulæ $C_{32}H_{43}NO_{10}$ and $C_{32}H_{43}NO_{11}$. A more detailed examination was made of a new specimen of alkaloïd which had been extracted by Mr. T. B. Groves from 1 cwt. of roots purchased in commerce as those of *Aconitum napellus.* From this crude alkaloid there were finally obtained two distinct alkaloïdal nitrates which furnished two bases, both soluble in ether, the one being deposited from its ethereal solution as a varnish which refused to crystallise. the other in distinct crystals. Both of these bases yielded crystalline salts. The uncrystallisable base did not produce the tingling of the tongue which is characteristic of aconitine. On account of its bitter taste, this alkaloid was called *picro-aconitine.* The name *aconitine* was reserved for the crystalline base.

The composition of picro-aconitine seems to be best expressed by the formula $C_{31}H_{45}NO_{10}$, and its crystalline hydrochloride by the formula $C_{31}H_{45}NO_{10},HCl + 1\frac{1}{2}H_2O$. The aurochloride,

$$C_{31}H_{45}NO_{10},HAuCl_4,$$

is a pale-yellow precipitate, very slightly soluble in water. The platinochloride (not analysed) is extremely soluble. This uncrystallisable alkaloïd was apparently not present in the root of *Aconitum napellus* with which Mr. T. B. Groves first worked.

The crystalline aconitine was burned after recrystallisation from ether. It gave numbers agreeing with the formula $C_{33}H_{45}NO_{11}$. Its properties were identical with those of the alkaloid first obtained by Mr. Groves, and also with the crystalline aconitine of Duquesnel. Further examination proved, however, that the alkaloïd was still contaminated with traces of impurity which repeated crystallisation from ether failed to remove. That this was the case was evident from the fact that its properties were changed by conversion into a salt, repeated crystallisation of the salt from water, and regeneration of the base from it. The regenerated base, after recrystallisation from ether, afforded the following results on combustion.

	Found.	Calculated for $C_{33}H_{43}NO_{12}$.
C	61·71 per cent.	61·39 per cent.
H	6·78 „	6·67 „

It would, therefore, appear that the formula of crystallised aconitine is $C_{33}H_{43}NO_{12}$. The hydrochloride and aurochloride were prepared and analysed. The latter salt is precipitated in pale-yellow flakes when auric chloride is added to a solution of aconitine hydrochloride. The amount of gold contained in the dried precipitate was ascertained to be 19·98 per cent.; that calculated for the formula $C_{33}H_{43}NO_{12},HAuCl_4$ is 19·92 per cent.

A fresh quantity of alkaloïd was now isolated by Messrs. Hopkin and Williams from 2 cwts. of root, Duquesnel's process being employed for the purpose. Resin was removed by extracting the acid liquid with light petroleum, and the alkaloïd precipitated with potassium carbonate in slight excess. The precipitate was removed. The alkaline filtrate was found still to contain alkaloïd, which was thrown out, after acidifying, with Mayer's reagent, and the base regenerated from the mercuric compound. It yielded some crystalline aconitine, but the greater part consisted of *uncrystallisable alkaloïd*, which furnished uncrystallisable salts, and hence was not picro-aconitine.

The precipitate thrown down by potassium carbonate was successively extracted with small quantities of ether, and the ethereal solutions agitated with solution of tartaric acid in order to remove alkaloïd, and leave in the ether a small quantity of resin. The acid liquid was precipitated with sodium carbonate, and the resulting alkaloïd collected and partially dissolved in ether. This ethereal solution deposited some slightly coloured crystals which were dissolved in benzene, and precipitated by adding light petroleum. This constituted the first specimen of *crystalline* alkaloïd. A second specimen was obtained from the ethereal mother liquors, which finally left a residue of uncrystallisable alkaloïd resembling that which had been dissolved by the alkaline liquid. On combustion, this amorphous substance afforded numbers which agreed approximately with those recorded by v. Planta, and from which he deduced the formula $C_{30}H_{47}NO_7$. It is probably a mixture.

The crystalline alkaloïd, after recrystallisation from ether, was converted into hydrobromide, and this salt crystallised from water. Specimens of alkaloïd regenerated from this compound were burned, and afforded the following results:—

	Mean result of the combustion of seven specimens.	Calculated for $C_{33}H_{43}NO_{12}$.
C	61·02 per cent.	61·39 per cent.
H	6·79 „	6·67 „

Another portion of crystalline alkaloïd gave C 61·41 per cent., H 6·81 per cent., which agreed better with the suggested formula. The alkaloïd melted at 183—184°, and formed a crystalline hydrobromide, $C_{33}H_{43}NO_{12},HBr + 2\frac{1}{2}H_2O$, and an aurochloride,

$$C_{33}H_{43}NO_{12},HAuCl_4.$$

The percentage of total alkaloïd in the root was about 0·07 per cent., of which 0·03 per cent. was crystalline aconitine, and 0·04 per cent. uncrystallisable base.

It appears from these results that the root of *Aconitum napellus* contains but one crystalline alkaloid. This had been obtained from each of the three separate batches of root examined. Picro-aconitine, the amorphous base yielding crystalline salts, had only been found in one parcel of roots, and would thus seem not to be a constant constituent. It may have originated from foreign root which was present in one of the collections of roots of *Aconitum napellus.*

Besides picro-aconitine, a second amorphous alkaloïd was isolated, which did not form crystalline salts. This substance was only found in one collection of roots, and seems to correspond with the alkaloïd of v. Planta. It may be a decomposition product of aconitine. The existence of a crystalline alkaloïd in the root of *Aconitum napellus* may be regarded as certain, but the occurrence of the two amorphous alkaloids above referred to requires confirmation.

The later results which Dr. Wright gained from an examination of *Aconitum ferox* and Japanese aconite root have rendered it probable that the different species of this plant yield distinct alkaloïds, and, in future work on this subject, it will therefore be necessary to carefully establish the homogeneity and exact source of the roots which are submitted to chemical investigation.

More recently the crystalline alkaloïd of *Aconitum napellus* has been examined by Jürgens (*Inaug. Dissert., Dorpat,* 1885). The origin of the roots used is not stated, and there is no evidence that they were carefully selected. They were extracted with alcohol, and the residue left by the alcoholic liquid, on evaporating it at first at 100°, and finally under reduced pressure at a low temperature was found to be acid, no foreign acid was therefore added. Resin having been removed by extraction with ether, the liquid was made alkaline with sodium hydrogen carbonate, and the alkaloid removed from it by repeated agitation with ether. The residue from the distillation of the ethereal solution was faintly acidified with a dilute solution of hydrogen chloride, and the liquid poured away from the insoluble brown resin.

By the addition of sodium hydrogen carbonate, the alkaloïd was liberated from the acid solution and dissolved from it by ether. The partly crystalline but coloured alkaloïd left on the evaporation of the ether, was converted into the hydrobromide, and the alkaloïd regenerated from this salt. By this means a colourless crystalline base was obtained, of which the root yielded as much as 0·2 per cent.

This alkaloïd melted at 179°, and afforded the following results when burned:—

	Mean result of three combustions.	Calculated for	
		$C_{33}H_{43}NO_{12}$.	$C_{33}H_{47}NO_{12}$.
C	61·16 p. c.	61·39 p. c.	61·02 p. c.
H	7·26 „	6·67 „	7·24 „

The mean result of four combustions showed that the substance contained 2·21 per cent. of nitrogen. The formula $C_{33}H_{43}NO_{12}$ corresponds with 2·17 per cent., whilst $C_{33}H_{47}NO_{12}$ corresponds with 2·16 per cent.

The aurochloride was produced as an amorphous, pale-yellow precipitate by the addition of auric chloride to a solution of the hydrochloride by the alkaloïd. This precipitate contained 19·84 per cent. of gold ($C_{33}H_{47}NO_{12},HAuCl_4$ = 19·8 per cent.). The salt was crystallised from a mixture of chloroform and ether. When heated, the crystals changed colour at 120° and melted at 140°.

From the quantitative results recorded above, Jürgens concludes that crystalline aconitine is best represented by the formula $C_{33}H_{47}NO_{12}$, which differs from that suggested by Wright in containing an additional four atomic proportions of hydrogen.

Jürgens determined the solubility of the alkaloïd in several liquids. He found that 1 gram of aconitine is dissolved by the following quantities of the respective liquids at 22—24°:—Ether (rel. dens., 0·728), 39·21 grams; ether (rel. dens., 0·720), 63·9 grams; alcohol (rel. dens., 0·7945 at 21°), 37·04 grams; alcohol (90° Tralles), 23·78 grams; light petroleum (rel. dens., 0·670) 2·806 grams; benzene, 5·5 grams; water, 726·4 grams.*

Duquesnel observed aconitine to be lævorotatory. The specimen examined by Jürgens was inactive in the form of a 3 per cent. alcoholic solution when examined in a layer 200 mm. long. The anhydrous hydrochloride in aqueous solution was strongly lævorotatory $[\alpha]_D = -35·89°$, from which result the specific rotation of the alkaloïd contained in the solution was calculated to be $[\alpha]_D$ −37·91°.

Besides the crystalline alkaloïd, Jürgens obtained from the roots two amorphous bases. One was found dissolved in the ethereal solution from which the greater part of the aconitine had crystallised out. After purification it formed a coloured varnish, which melted below 100°. When boiled with alcoholic soda, it yielded benzoic acid and an amorphous base resembling the aconine of Wright. A combustion of the original substance showed it to contain of carbon 67·74 per cent., of hydrogen 8·4 per cent.

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* In a determination of the solubility of the aconitine with which we have worked, made in this laboratory by Mr. J. C. Umney, it was found that nearly ten times this quantity of water was required.

The second amorphous alkaloïd was nearly insoluble in ether, but dissolved readily in chloroform, by means of which solvent it was isolated from the original alkaline liquid, after it had been completely extracted with ether. It seems likely that this substance may have been impure aconine, the product of the hydrolysis of aconitine.

The Properties of Crystalline Aconitine from Aconitum Napellus.

The alkaloïd which we have examined is an indistinctly crystalline powder having a yellowish-brown tint. The mode in which it was obtained is described in a paper by Mr. John Williams, read at the meeting of the British Pharmaceutical Conference, in 1887 (*Pharm. J. Trans.* [3], 18, 238).* The coarsely ground root dried at a low temperature, was exhausted with amyl alcohol, a solvent which was found to be capable of readily dissolving the alkaloïdal salts contained in the root. The solution was shaken with dilute sulphuric acid, and the acid liquid precipitated with sodium carbonate. The precipitate thus obtained was crystallised from ether. Mr. Williams states that besides the crystalline alkaloid, nothing was isolated by this method except a minute quantity of "gummy amorphous" alkaloïd, which remained obstinately attached to the crystals.

Our first experiments were made with the indistinctly crystalline powder above referred to. This melted at 188·4° (corr.), and dissolved readily in chloroform and benzene, less readily in alcohol and ether, and hardly at all in light petroleum. It crystallised best from a mixture of alcohol and ether, and by this means large, perfect crystals were obtained, forming tabular prisms belonging to the rhombic system. The crystals had a faint yellow tinge, and those last obtained from the alcoholic liquid were slightly contaminated with the amorphous, gummy substance to which Mr. Williams has alluded as being so difficult to remove.

The results of two combustions of the original material were—

	Found.		Calculated for		
	I.	II.	$C_{33}H_{43}NO_{12}$.	$C_{33}H_{45}NO_{12}$.	$C_{33}H_{47}NO_{12}$.
C	61·31	61·51 p. c.	61·39	61·19	61·11 p. c.
H.....	7·67	7·58 „	6·67	6·95	7·26 „

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* We are indebted for a supply of this very valuable material to the liberality of Messrs. Howards & Sons, of Stratford.

These numbers agree fairly well with Wright's formula, but the substance burned was known to be slightly impure. The alkaloïd furnished well crystallised salts, from which pure alkaloïd was regenerated. The aurochloride was thrown down as a pale-yellow, amorphous precipitate (m. p. 120°), when auric chloride was added to an aqueous solution of the hydrochloride, but was readily crystallised from its alcoholic solution. The properties of this salt were carefully studied, with a view to its employment as a means of characterising the pure alkaloïd. It is readily soluble in absolute alcohol, chloroform, acetone, and methyl alcohol, less readily in ether and dilute alcohol. It is very sparingly soluble in water and dilute hydrochloric acid. The alcoholic solution does not decompose when heated, except in the presence of much water.

The crystals melted at about 135° (corr.). In order to ascertain the melting point of the pure aurochloride, a considerable quantity of that prepared from the original alkaloïd was fractionally crystallised from absolute alcohol, the crystallisation being facilitated by the successive addition of small quantities of water. When evaporation was necessary, it was effected in a vacuous desiccator over calcium chloride. The melting point of each fraction of crystals was ascertained, with the following results:—(1) 135°; (2) 135°; (3) 134°; (4) 135·6°; (5) 135°; (6) 132°. Each of these numbers represents the mean of three determinations. Since no distinct separation was effected by this means, a solution of the hydrochloride was fractionally precipitated with auric chloride, each precipitate was crystallised from alcohol, and the melting points of the different crystals taken. These were (1) 129°; (2) 135°; (3) 135°; (4) 135°. The first precipitate was very small, and evidently contained nearly the whole of the impurity with which the original alkaloïd was contaminated In order to ascertain whether the gold salt melting at 135° was pure aconitine aurochloride, seven specimens of it, obtained in this and the preceding experiments, were burned with lead chromate. The mean result of these seven combustions was, carbon, 41·56 per cent.; hydrogen, 5·35 per cent.; gold, 19·66 per cent. A separate determination of chlorine gave 13·85 per cent. These numbers do not agree well with any of the probable formulæ for the alkaloïd.

		Calculated for	
	Found.	$C_{33}H_{43}NO_{12}.HAuCl_4$.	$C_{33}H_{47}NO_{12}.HAuCl_4$.
C....	41·56 per cent.	40·2	40·08 per cent.
H...	5·35 „	4·36	4·75 „
Au..	19·66 „	19·92	19·8 „
Cl...	13·85 „	14·43	14·34 „

It therefore appeared likely that the aurochloride melting at 135°

was still contaminated with an impurity richer in carbon, no doubt the same impurity (or its aurochloride) as that associated with the original substance.

The experiments recorded above had shown that on adding auric chloride to a solution of the impure hydrochloride the impurity is precipitated first. Since the amount of this second substance is very small, we repeated the experiment of fractional precipitation, using a larger quantity of alkaloïd in the hope of obtaining from the later fractions aconitine aurochloride in a pure state. Ten grams of the original material were converted into hydrochloride, and sufficient auric chloride was added to precipitate about one-fifth of the base. The precipitate was filtered off and the remaining 8 grams of alkaloïd recovered from the filtrate in the usual way. From a solution in a mixture of ether and alcohol the alkaloïd crystallised in large, flat, rhombic prisms, some of which were very perfect. These crystals have been measured, and their crystallographic characters described by Mr. A. E. Tutton (see p. 288), to whom our best thanks are due. They melted at 188·5° (corr.), and yielded an aurochloride which, after crystallisation from alcohol and drying over calcium chloride, melted at 135·5° (corr.). On combustion this compound, dried at first in a vacuum over calcium chloride and finally at 100°, afforded the following data :—

		Calculated for	
	Found.	$C_{33}H_{45}NO_{12},HAuCl_4$.	$C_{33}H_{43}NO_{12},HAuCl_4$.
C ..	40·16 per cent.	40·12	40·2 per cent.
H ..	4·56 „	4·55	4·36 „
Au .	19·8 „	19 96	19·92 „

We have since prepared this aurochloride (m. p. 135·5°) from various specimens of aconitine salts obtained in the course of the investigation, and there can be no doubt that it is a pure substance.

From the aurochloride, the pure alkaloïd was regenerated by the following method, the only one which proved successful out of a large number that were tried; the addition of any alkali to aconitine aurochloride causes oxidation of the alkaloïd and consequent precipitation of metallic gold. The salt is finely ground with water in which it is nearly insoluble, and aqueous hydrogen sulphide is added drop by drop until all the compound has been changed to auric sulphide, and a faint smell of hydrogen sulphide remains permanent; the addition of excess of the precipitant should be avoided. The solution is then filtered, and, if necessary, a slow current of air passed through it to remove any hydrogen sulphide it may contain. Sodium hydrogen carbonate is then added in slight excess, and the liquid extracted with ether.

On combustion, the crystalline base thus recovered from the pure aurochloride and dried at 100°, gave the following result, which is the mean of two determinations :—

		Calculated for	
	Found.	$C_{33}H_{45}NO_{12}$.	$C_{33}H_{43}NO_{12}$.
C	61·17 per cent.	61·20	61·39 per cent.
H	7·07 ,,	6·95	6·67 ,,

Burned in a Sprengel vacuum with a mixture of copper and copper oxide, 2·2 per cent. of nitrogen was obtained; the formula $C_{33}H_{45}NO_{12}$ requires 2·16 per cent.

Since the crystalline aurochloride can readily be produced even from small quantities of material, and has a definite melting point, its production constitutes a reliable means of identifying aconitine, whilst the pure alkaloid can easily be regenerated from the aurochloride and obtained in a crystalline state for examination.

We find that aconitine itself, as well as its hydrochloride, is able to combine with gold chloride. This compound, which crystallises well, is obtained by mixing together ethereal or alcoholic solutions of aconitine and auric chloride and concentrating the liquid. Except in presence of excess of auric chloride, crystals separate as the liquid evaporates, but should they not do so the solution is precipitated with water to remove gold chloride, and the precipitate crystallised from alcohol. As this compound is extremely soluble in alcohol and insoluble in water, it may readily be fractionally crystallised from its alcoholic solution by the successive additions of small quantities of water followed by slow evaporation in a desiccator. These remarks also apply to the true aurochloride of the alkaloid.

The crystals of the new compound melt at 129°, that is, 6·5° lower than the aurochloride containing hydrochloric acid. The mean result of two combustions of the dry crystals for carbon and hydrogen, and of two determinations of gold and chlorine, were

		Calculated for	
	Found.	$C_{33}H_{45}NO_{12},AuCl_3$.	$C_{33}H_{43}NO_{12},AuCl_3$.
C	41·79	41·7	41·8 per cent.
H	5·30	4·74	4·54 ,,
Au......	20·4	20·65	20·7 ,,
Cl	10·9	11·21	11·24 ,,

This compound, which we shall call *aconitine gold chloride*, is more stable in solution, especially in presence of water, than the true aurochloride. This greater stability may be partly due to the absence of hydrochloric acid, which readily induces hydrolysis of the alkaloid.

Aconitine from *Aconitum napellus* is distinguished by its crystalline character and that of its salts. It may be identified by its melting point (188·5°, corr) and by the formation of a gold salt from the base itself, as well as from the hydrochloride, the aurochloride

$$(C_{33}H_{45}NO_{12},HAuCl_4)$$

melting at 135·5° (corr.), and the aconitine gold chloride

$$(C_{33}H_{45}NO_{12},AuCl_3)$$

melting at 129° (corr.). The pure base can be regenerated without difficulty from either of these compounds.

Great discrepancy exists among the numbers which have been recorded as the melting point of aconitine. Duquesnel gives 140°, Wright 183—184°, Jurgens 179°. The alkaloid examined by Duquesnel appears from Wright's results to have been impure. The want of concordance of our result (188 5°) with those of Wright and Jürgens may be due, apart from different states of purity and differences in the methods of determination, to the circumstance that if aconitine is slowly heated it melts at a lower temperature than if quickly heated. Our practice has been to determine the melting point in a bath of paraffin long enough to entirely immerse the stem of the thermometer. The paraffin is heated to about 150° before the thermometer, with the thin glass tube attached to it, is immersed. During the whole operation the liquid is well stirred. The results obtained in this way are very concordant.

As regards the composition of aconitine, our data agree best with the formula $C_{33}H_{45}NO_{12}$, which contains two atomic proportions of hydrogen more than that suggested by Wright and Luff ($C_{33}H_{43}NO_{12}$), and two atomic proportions of hydrogen less than the formula proposed by Jurgens, ($C_{33}H_{47}NO_{12}$). For convenience of reference, we tabulate here the composition of aconitine as determined by Wright and Luff, by Jürgens, and by ourselves, together with that calculated from the three formulæ. In each instance the experimental result is the mean of several determinations.

	Found.		
	Wright and Luff.	Jurgens.	Dunstan and Ince.
C	61·21	61 16	61·17 per cent.
H	6 80	7 26	7 07 „

	Calculated for		
	$C_{33}H_{43}NO_{12}$.	$C_{33}H_{45}NO_{12}$.	$C_{33}H_{47}NO_{12}$.
C	61·39	61 20	61·02 per cent.
H	6 67	6·95	7 24 „

The nitrogen determinations are not recorded, as they do not help to decide between these formulæ, owing to the small amount of this element which is contained in the substance. The agreement between the three sets of results is very striking; they differ, in fact, only within the limits of experimental error. Jürgens' numbers agree better with the formula to which our results have led us, namely, $C_{33}H_{45}NO_{12}$, than with that he has deduced from them, ($C_{33}H_{47}NO_{12}$), whilst the data obtained by Wright and Luff are also in close approximation to it. Our analyses of the aurochloride likewise agree with the formula containing 45 atoms of hydrogen. It should be remarked, however, that even when every possible refinement is practised in the process of combustion, it is doubtful whether the operation is competent to detect a difference of two atomic proportions of hydrogen in such a large molecule as that of aconitine. Taking all circumstances into account, however, $C_{33}H_{45}NO_{12}$ seems to us most likely to be the correct formula.

Specific Rotation of Aconitine.

Duquesnel states that aconitine is lævorotatory. Jürgens found 3 per cent. alcoholic solution to be inactive when examined in a layer 200 mm. long. He observed, however, the hydrochloride in aqueous solution to be strongly lævorotatory $[\alpha]_D = -35{\cdot}89^\circ$.

The crystalline alkaloïd examined by us is markedly *dextro-rotatory*. A 3 per cent. alcoholic solution afforded the following results with Laurent's large "half-shade" instrument:—

a. [23°] + 0·66°; *l.* 2 dm.; *p.* 3·726 gram; *d.* 25°/25°, 0·805.

whence, $$\frac{100 \times 0{\cdot}66}{2 \times 3{\cdot}726 \times 0{\cdot}805} = [\alpha]_D + 11{\cdot}01.$$

Another determination with a second specimen of purified alkaloïd gave

a. [20°] + 0·81°; *l.* 2 dm.; *c.* 2·7464,

whence, $$\frac{100 \times 0{\cdot}81}{2{\cdot}7464 \times 2} = [\alpha]_D + 11{\cdot}10^\circ.$$

The crystalline hydrobromide ($C_{33}H_{45}NO_{12},HBr,2\frac{1}{2}H_2O$) was next examined.* Its aqueous solution was found to be strongly *lævorotatory*.

a. [20°] − 3·25°; *l.* 2 dm.; *c.* 5·1832,

whence, $$\frac{100 \times 3{\cdot}25}{5{\cdot}1832 \times 2} = [\alpha]_D - 31{\cdot}3^\circ.$$

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* This salt had been prepared by Dr. C. R. A. Wright. It is one of a number of specimens of aconitine compounds which he has very kindly placed at our disposal.

The hydrobromide prepared from the alkaloid now under investigation and recrystallised several times from water, likewise proved to be lævo-rotatory in aqueous solution, giving a result which agrees with that obtained from Dr. Wright's specimen.

a. [20°]—1·2°; *l.* 2 dm.; *d.* 20°/20°, 1·0098; *p.* 1·95 gram,

whence, $$\frac{100 \times 1 : 2}{2 \times 1{\cdot}95 \times 1{\cdot}0098} = [\alpha]_D - 30{\cdot}47^\circ.$$

This hydrobromide was now reconverted into the alkaloïd, and its specific rotation again determined in alcoholic solution. The following result was obtained, which confirms the correctness of our previous determinations.

a. [20°] 0·35°; *l.* 2 dm.; *d.* 20°/20°, 0·8074; *p.* 2·07,

whence, $$\frac{100 \times 0{\cdot}35}{2 \times 2{\cdot}07 \times 0{\cdot}8074} = [\alpha]_D + 10{\cdot}47^\circ.$$

These results furnish conclusive proof of the remarkable fact that, whilst the alkaloïd is dextro-rotatory, its hydrobromide is lævo-rotatory.

Effect of Heat on Aconitine.

In order to ascertain whether aconitine is decomposed when it is heated, the following experiments were made. A weighed quantity of the alkaloïd (0·1991 gram) was heated for 2½ hours at 100° in a vacuum; the loss only amounted to 0·0004 and the crystalline alkaloïd was readily recovered unchanged. The same quantity of alkaloïd was now heated at 120° for two hours in a vacuum; it lost 0·0008 gram and was little if at all altered. In a third experiment, the same amount of substance was heated until it melted (185—188°), and was kept at this temperature for one hour. The resulting brown varnish weighed 0·1789 gram, that is to say, there had been a loss of about 10 per cent. This substance dissolved almost completely in dilute hydrochloric acid. On regenerating the base from the acid liquid by the addition of sodium hydrogen carbonate, and extracting the alkaline liquid with ether, no crystalline alkaloïd, but only an amorphous varnish was obtained. This was dissolved in dilute hydrochloric acid and precipitated with auric chloride. From this salt, which refused to crystallise, the base was regenerated as a varnish. The amount of loss which occurred under these conditions, corresponds approximately with that sustained in the conversion of aconitine, $C_{33}H_{45}NO_{12}$, into aconine, $C_{26}H_{41}NO_{11}$, benzoic anhydride being volatilised. The properties of the uncrystallisable base agree with those of aconine.

It appears from these experiments that although aconitine is almost completely decomposed when heated at its melting point, it is not altered by exposure to a temperature of 100—120°.

Experiments were also made to ascertain whether aconitine is decomposed when heated with water or with weak alkaline solutions. About half a gram of aconitine was boiled with about 10 times its weight of water for four hours. The liquid was then acidified and extracted with ether which, however, removed next to nothing. On the addition of sodium hydrogen carbonate in excess to the acid liquid, nearly the whole of the alkaloïd was recovered by extraction with ether, and was left in crystals on the evaporation of the solvent. Further experiments proved that in presence of much larger quantities of water, more than sufficient to dissolve the alkaloïd, and after much longer boiling, appreciable quantities of aconitine are resolved into aconine and benzoic acid. Wright and Luff have shown that aconitine is completely decomposed into aconine and benzoic acid by prolonged heating with water in a closed tube at 100°.

When aconitine is boiled for three hours with water rendered alkaline with ammonia there is more change than with water alone, a small proportion of the alkaloïd being resolved into aconine. The greater part of the aconitine may, however, be recovered. Solutions of potassium and sodium carbonates were found to act more powerfully, some action occurring even in the cold after prolonged standing, whilst on boiling, nearly the whole of the alkaloïd is decomposed into aconine and benzoic acid. Wright and Luff have shown that the caustic alkalis rapidly effect the same decomposition, especially when they are used in alcoholic solution. The mineral acids, particularly hydrochloric acid, induce a similar change.

Formation and Properties of Apo-aconitine or Anhydro-aconitine.

Wright and Luff observed the action of dilute mineral acids to consist, in the first instance, in the splitting off of 1 mol. prop. of water, a new base being formed, to which they gave the name "apo-aconitine," but for the sake of uniformity in chemical nomenclature, this substance should be called anhydro-aconitine, or dehydraconitine,*

$$(C_{33}H_{45}NO_{12} = C_{33}H_{43}NO_{11} + H_2O).$$

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* Since the compound is produced by the *dehydration* of aconitine, the name "dehydraconitine" would seem to be best, and several substances having a similar origin are so named, *e.g.*, dehydracetic acid. On the other hand, it may be convenient to designate a body derived from aconitine by loss of hydrogen "dehydraconitine." We, therefore, call this alkaloïd "anhydro-aconitine." The name "Apo-aconitine" does not connote the relationship of the compound to aconitine.

When mineral acids are employed, this dehydration is rapidly followed by hydrolysis, and the base aconine is formed, together with benzoic acid. If, however, the aconitine is heated with a strong solution of tartaric acid, dehydration takes place exclusively, and the anhydro-base alone is produced. The existence of this compound has been questioned by later workers, but no experimental proof of its non-existence has been adduced. The results we have obtained place the identity of this alkaloïd beyond doubt.

Aconitine was heated at 100° with a saturated solution of tartaric acid in a sealed tube for six hours. On recovering the alkaloïd, it was evident that it still contained aconitine. The operation was therefore repeated for four hours longer at 100—110°. No darkening occurred, and ether extracted nothing appreciable from the acid liquid. The base was obtained by agitating the solution with ether after it had been made alkaline with sodium hydrogen carbonate. The colourless ethereal solution left, on spontaneous evaporation, small colourless crystals which melted at 186·5° (corr.),* that is 2° lower than aconitine. Unlike aconitine, this alkaloïd cannot be obtained in large crystals from its solution in a mixture of alcohol and ether, but is invariably deposited in minute crystals which cohere together and stick to the glass vessel. In most respects it closely resembles the parent alkaloïd. The following is the mean result of two combustions of the substance:—†

	Found.	Calculated for $C_{33}H_{43}NO_{11}$.
C	63·01 per cent.	62·97 per cent.
H	6·98 „	6·87 „

Anhydro-aconitine, like aconitine, forms crystalline salts. We have also obtained a compound of gold chloride with the base, as well as with the hydrochloride.

The *aurochloride* has remarkable properties. It is thrown down as an amorphous precipitate when auric chloride is added to a solution of the hydrochloride of the alkaloïd. This was readily crystallised from an alcoholic solution, the resulting crystals melting at 133°. In order to determine whether the compound was homogeneous, the crystals were dissolved in absolute alcohol, and fractionally precipitated in the manner described in connection with the aurochloride of aconitine. Two fractions were obtained; the first melted at 135°, and seemed to be identical with aconitine aurochloride, the second fraction melted at 129·5°. It seemed probable that the first fraction consisted of the corresponding aconitine compound, regenerated by the action of water, whilst the second fraction might be the aurochloride of anhydro-aconitine. To ascertain whether this was the case, a fresh quantity of the aurochloride was precipitated and dissolved in absolute alcohol, and the solution was evaporated in a vacuous desiccator over calcium chloride until crystallisation commenced. The crystals obtained differed from both those previously obtained in melting at 141°. They were shown by analysis to be the true aurochloride of anhydro-aconitine—

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* Wright and Luff record 185—186° as the melting point (? uncorrected).

† The analytical data recorded by Wright and Luff do not agree with the formula they suggest, $C_{33}H_{41}NO_{11}$, the hydrogen being 1 per cent. too high.

	Found.	Calculated for $C_{33}H_{43}NO_{11},HAuCl_4$.
C	40·8 per cent.	40·68 per cent.
H	4·58 ,,	4·56 ,,

Another portion of the precipitated aurochloride was also dissolved in absolute alcohol, and was caused to crystallise by the addition of water. The crystals thus prepared melted at 129°. Analysis proved them to be an isomeride of aconitine aurochloride, in all probability the hydrate of the aurochloride of anhydro-aconitine:—

	Found.	Calculated for $C_{33}H_{43}NO_{11},HAuCl_4,H_2O$.
C	40·01 per cent.	40·12 per cent.
H	4·59 ,,	4·55 ,,

It was suspected that this compound might readily change into the isomeric aurochloride of aconitine, and this suspicion was found to be justified. On recrystallising the substance from dilute alcohol, crystals were obtained melting at 135 5°, which analysis proved to be aconitine aurochloride—

	Found.	Calculated for $C_{33}H_{45}NO_{12},HAuCl_4$.
C	40·08 per cent.	40 12 per cent.
H	4·66 ,,	4·55 ,,

Anhydro-aconitine is thus shown to form an aurochloride melting at 141°. This, in presence of water, yields a hydrated compound melting at 129°, which readily changes into the isomeric aconitine aurochloride melting at 135·5°.

Anhydro-aconitine gold chloride is prepared by mixing alcohol or ethereal solutions of the alkaloïd and auric chloride. On evaporation, crystals are deposited which melt at 147·5°, and are not altered by recrystallisation from alcohol. This compound shows no tendency to pass into the corresponding aconitine salt. Its crystals dried at 100°, were burned with the following results:—

	Found.	Calculated for $C_{33}H_{43}NO_{11}\cdot AuCl_3$.
C	42·25 per cent.	42 28 per cent.
H	4 76 „	4·62 „

Aconine.

Aconine is the name given by Wright and Luff to the product of the hydrolysis of aconitine by mineral acids and alkalis. It is formed, together with benzoic acid, in accordance with the equation $C_{33}H_{43}NO_{12} + H_2O = C_{26}H_{39}NO_{11} + C_7H_6O_2$. Aconine is an uncrystalline base, and its salts are also uncrystalline.

The crystallised aconitine which we have examined yielded, on hydrolysis, an amorphous base which is evidently identical with aconine.

Aconitine was boiled for some hours with alcoholic potash. The alcohol was then distilled off, the liquid acidified with hydrochloric acid, and extracted with ether. The ethereal solution was shaken with dilute alkali to remove the acid product of hydrolysis. After this treatment, the ethereal solution was evaporated to dryness, leaving a resinous substance which appears to result from a further action of alkali on aconine. The acid was regenerated from its salt, and, after recrystallisation, melted at 120·6° (corr). Benzoic acid melts at 121°. The silver salt was prepared in the usual way, and analysed.

I. 1·1824 gram of salt gave 0 08886 gram of silver = 47·09 per cent.

II. 2·5366 gram of salt gave 0·1194 gram of silver = 47 08 per cent.

Calculated for $AgC_7H_5O_2$ = 47·17 per cent.

The acid solution which had been extracted with ether was now made alkaline, and extracted with chloroform, aconine being insoluble in ether. From this solution was obtained a brown resinous base. By fractionally precipitating a solution in chloroform with ether or light petroleum, the alkaloïd is obtained as a last fraction nearly free from colour, but still resinous and friable when dry. It was soluble in water and alcohol, but insoluble in ether, benzene, and light petroleum. All attempts to crystallise it were failures. No crystalline salt could be obtained. Aqueous solutions of the alkaloid or its salts were precipitated by the usual alkaloïdal reagents, but no crystalline derivative or compound could be prepared.

The aurochloride is a pale-yellow, amorphous precipitate which dissolves in alcohol, and is deposited as the solution evaporates in oleo-resinous films. Contrary to the experience of Wright and Luff, we find this compound, when prepared from pure aconine, to be quite as stable, or even more stable, than the corresponding aconitine salt.

Two combustions were made of the amorphous base dried at 100°, the mean result was

	Found.	Calculated for $C_{26}H_{41}NO_{11}$.
C	56·97 per cent.	57·44 per cent.
H	8·17 „	7·73 „

The amorphous aurochloride dried at 100° gave the following results on combustion :—

	Found.	Calculated for $C_{26}H_{41}NO_{11},HAuCl_4$.
C	34·9 per cent.	35·33 per cent.
H	5·09 „	4·75 „
Au............	22·7 „	22·31 „

These analyses of aconine furnish confirmation of the correctness of the formula $C_{33}H_{45}NO_{12}$ for aconitine, from which the amorphous base is formed in accordance with the equation $C_{23}H_{45}NO_{12} + H_2O = C_{26}H_{42}NO_{11} + C_7H_6O_2$.

The results recorded in the present communication serve to establish the characteristic properties of the principal and doubtless the most poisonous alkaloïd of *Aconitum napellus*, and render its future identification comparatively easy. In order to throw light on the nature of the other alkaloïds contained in this plant, if other alkaloïds there be, an investigation is being made of some valuable roots obtained from specially selected plants.

Our thanks are due to Dr. F. W. Passmore for the assistance he has given us, particularly in verifying and extending some of the later observations recorded in this paper, our further co-operation in carrying on this work being prevented through one of us having been obliged to leave London to take up a provincial appointment.

Research Laboratory of the
Pharmaceutical Society,
London.

XXXI.—*Crystallographical Characters of Aconitine from* Aconitum napellus.

By Alfred E. Tutton, Assoc. R.C.S., Demonstrator in Chemistry at the Royal College of Science, London.

The crystals of aconitine obtained during the course of the work described in the preceding communication were frequently of considerable size, and generally well developed. The specimens examined were transparent prisms, terminated by pyramids. They were of a faint yellowish colour, with a brilliant lustre, and varied in size from very small to prisms a centimetre long, and half a centimetre thick. One of the prism faces was sometimes so much better developed than the others as to give the crystals an elongated tabular appearance. Excellent reflections, as a rule, were obtained, but occasionally the images were distorted by a slight curvature of the faces.

Eight crystals were measured as completely as their development would permit.

System: Rhombic. Habit: Prismatic with an inclination to tabular, owing to large development of the brachypinacoid.

Ratio of axes: $a : b : c = 0{\cdot}5456 : 1 : 0{\cdot}3885$.

Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\breve{P}\infty$;
$p = \{110\}\infty P$ $p' = \{120\}\infty\breve{P}2$;
$m = \{101\}\bar{P}\infty$; $q = \{021\}2\breve{P}\infty$;
$o = \{121\}2\breve{P}2$.

The general appearance of the crystals is shown in Fig. 1, and their spherical projection in Fig. 2.

Fig. 1.

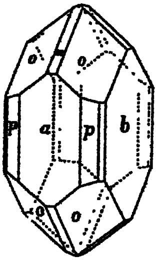
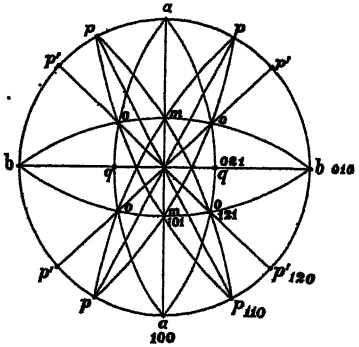


Fig. 2.



The brachypinacoid *b*(010) is the best developed face. The orthopinacoid *a*(100) is also generally well developed, but is almost invariably narrower than *b*. The primary prism faces *p*(110) are always present, often as broad as the orthopinacoid, but occasionally mere lines. The prism *p′*(120) was only once observed, and gave but a very faint image. Of the end faces, the pyramid *o*(121) is always largely developed, and gives excellent reflections. The primary macrodome *m*(101) is usually developed to about the extent shown in the drawing, but is sometimes narrower, and occasionally absent. The brachydome *q*(021) was only once observed, and the image was then faint and distorted.

The following goniometrical measurements were made :—

Angle observed.	No of measurements.	Limits.	Mean observed.	Calculated.
bp = 010 : 110	24	60° 43 — 62° 21′	61° 16′	61° 23′
pa = 110 : 100	21	27 6 — 29 21	28 44	28 37
bp′ = 010 : 120	1	—	42 53	42 30
bo = 010 : 121	44	56 36 — 58 23	57 42	*
om = 121 : 101	36	31 24 — 32 49	32 18	32 17
am = 100 : 101	16	54 10 — 54 50	54 27	54 33
mm = 101 : $\bar{1}01$	5	70 52 — 71 12	71 3	70 54
ao = 100 : 121	41	59 32 — 61 39	60 39	*
oq = 121 : 021	2	29 3 — 29 30	29 17	29 21
oo = 121 : $\bar{1}21$	18	57 40 — 59 24	58 35	58 42
pm = 110 : 101	31	58 41 — 60 18	59 20	59 23
mo = 101 : $\bar{1}21$	32	73 4 — 74 51	73 58	73 57
op = $\bar{1}21$: $\bar{1}\bar{1}0$	36	46 4 — 47 14	46 37	46 40
bq = 010 : 021	1	—	51 40	52 10

The two most frequently measured angles *bo* and *ao* were taken as basis of the calculations. In the most perfectly developed crystals, the rhombic nature of the symmetry was very evident, the angles upon opposite sides of the symmetry planes being identical within a very few minutes. The optical properties, however, conclusively prove the truly orthorhombic character of the crystals.

There is a good cleavage parallel to the macropinacoid *a*(100), the *a* axis being the direction of minimum cohesion.

The optic axial plane is the brachypinacoid *b*(010). Through the macropinacoid *a*(100) both axes are seen in convergent light, symmetrically placed with respect to the normal to the face, separated at their acute angle. The axis *a* is thus the first median line. The rings and lemniscates are best seen through sections parallel to *a*, about 1½ mm. in thickness. For the purpose of measurement, three crystals with an *a* face well developed were chosen; they were cemented by the *a* face in the usual manner upon a thin glass plate, and then carefully ground in oil until they had been reduced to the right thickness. This mode of preparing sections was found preferable to using cleavage plates, as the latter were always more or less distorted. A section perpendicular to the second median line was also cut, but the obtuse angle was not visible in oil.

Aconitine, as will be seen from the following measurements, is a somewhat highly dispersive substance. The hyperbolic brushes are deeply fringed with colour, and a considerable difference is observed between the positions of the axes for different rays of the spectrum.

The following values were obtained for the apparent acute optic axial angle in air 2E as the mean of a large number of measurements with the three distinct sections referred to :—

For lithium light	47°	0′
For sodium light.................	56	10
For thallium light	65	5

The dispersion between these limits is thus seen to be 18° 5′ of the nature $\rho < v$. The whole of the values obtained were very near the mean values above given. The sections employed gave the interference figures very clearly. The larger axial angle apparatus of Fuess was used in making the measurements.

The sign of double refraction, determined by means of a quarter undulation mica plate, is positive.

In an inaugural dissertation at Dorpat, in 1885, Jürgens briefly described some crystals of aconitine as belonging to the rhombic system, and exhibiting the faces of the macropinacoid, primary prism, and brachydome. No measurements, however, were given.

XXXII.—*Molecular Refraction and Dispersion of various Substances.*

By J. H. Gladstone, Ph.D., F.R.S.

Since the paper on the refraction equivalents of the elements, published in the *Phil. Trans.* of 1879, a considerable number of observations of refractive indices have accumulated in my note books, besides those which have been published from time to time. It seems desirable to make a permanent record of such as may be valuable in determining the optical constants.

Effect of Change of Temperature.

Amongst the earliest of these unpublished observations are some that were made to determine how far the law holds good that the specific refractive energy of a body is unaffected by temperature. The method employed was that of determining the refraction for different lines of the spectrum on a hot summer's day, preserving the specimen carefully until the following winter, and then redetermining it. I give only those made upon bisulphide of carbon and benzene, as they are substances referred to in the paper by Dale and myself, in the *Phil. Trans.* of 1863, and the present observations may be regarded as more exact than those given therein.

Bisulphide of Carbon.

Temp. C.	Density.	μ_A.	μ_B.	μ_C.	μ_D.	μ_E.	μ_F.	μ_G.	μ_H.
10·0°	1·2793	1·6153	1·6217	1·6250	1·6344	1·6471	1·6592	1·6837	1·7078
24·5	1·2593	1·6045	1·6109	1·6143	1·6235	1·6362	1·6483	1·6722	1·6954
1·5	1·2909	1·6227	1·6288	—	1·6417	—	1·6672	—	1 7159
23·0	1·2594	1·6070	1·6134	—	1·6260	—	1·6504	—	1·6972
30·0	1·2494	1·6026	1·6087	—	1·6213	—	1·6458	—	1·6922

Benzene.

Temp. C.	Density.	μ_A.	μ_B.	μ_C.	μ_D.	μ_E.	μ_F.	μ_G.	μ_H.
10·0°	0·8868	1·4935	1·4965	1·4983	1·5029	1·5091	1·5148	1·5258	1·5355
21·5	0·8773	1·4887	1·4917	1·4934	1·4979	1·5040	1·5095	1·5205	1·5304
2·0	0·8979	1·5021	1·5053	—	1·5122	—	1·5242	—	1·5460
23·7	0·8760	1·4893	1·4928	—	1·4993	—	1·5109	—	1·5320
28·6	0·8709	1·4860	1·4897	—	1·4960	—	1·5094	—	1·5279

The first two lines in each case represent one specimen, and the three following another specimen.

The following tables give the refractive index divided by the density, or, in other words, the specific refractive energy:—

Bisulphide of Carbon.

Temp. C.	$\frac{\mu_A - 1}{d}$.	$\frac{\mu_B - 1}{d}$.	$\frac{\mu_C - 1}{d}$.	$\frac{\mu_D - 1}{d}$.	$\frac{\mu_E - 1}{d}$.	$\frac{\mu_F - 1}{d}$.	$\frac{\mu_G - 1}{d}$.	$\frac{\mu_H - 1}{d}$.
10·0°	0·4809	0·4859	0·4885	0·4959	0·5058	0·5153	0·5344	0·5532
24·5	0·4803	0·4851	0·4878	0·4951	0·5053	0·5148	0·5338	0·5522
1·5	0·4824	0·4871	—	0·4971	—	0·5168	—	0·5546
23·0	0·4820	0·4871	—	0·4971	—	0·5164	—	0·5536
30·0	0·4823	0·4872	—	0·4973	—	0·5169	—	0·5540

Benzene.

Temp C.	$\frac{\mu_A - 1}{d}$.	$\frac{\mu_B - 1}{d}$.	$\frac{\mu_C - 1}{d}$.	$\frac{\mu_D - 1}{d}$.	$\frac{\mu_E - 1}{d}$.	$\frac{\mu_F - 1}{d}$.	$\frac{\mu_G - 1}{d}$.	$\frac{\mu_H - 1}{d}$.
10·0°	0·5564	0·5598	0·5619	0·5670	0·5740	0·5804	0·5929	0·6038
21·5	0·5570	0·5604	0·5624	0·5675	0·5745	0·5807	0·5933	0·6046
2·0	0·5592	0·5628	—	0·5704	—	0·5838	—	0·6081
23·7	0·5585	0·5626	—	0·5700	—	0·5832	—	0·6073
28·6	0·5580	0·5623	—	0·5695	—	0·5849	—	0·6062

These tables serve to confirm the conclusion arrived at by Dale and myself, in 1863, and now generally received, that "the specific refractive energy of a liquid is a constant not affected by temperature." We considered at that time that "there is some influence * * * which gives rise to the slight progression of most of the calculated products;" this is generally believed to be the case, but the differences in the above tables may be attributable simply to experimental error.

Carbon Compounds.

The following table gives observations on various carbon compounds. Those marked with an asterisk are from specimens kindly furnished me by Dr. Perkin:—

Substance.	Formula.	Temp. C.	Density.	μ_A.	μ_D.	μ_F.	μ_H.
Pentane............	C_5H_{12}........	6·5°	0·6365	1·3607	1·3649	—	1·3769
Heptane	C_7H_{16}.......	12·0	0·6895	1·3875	1·3917	1·3966	1·4046
„	„	23·0	0·6809	1·3826	1·3867	1·3917	1·3991
„	„	7·6	0·6935	1·3904	—	1·3995	1·4073
Amylene*	C_5H_{10}........	20·2	0·6568	1·3776	—	1·3887	1·3991
Benzene*	C_6H_6	18·5	0·8815	1·4927	1·5027	1·5144	1·5357
Toluene............	C_7H_8.......	24·1	0·8566	1·4800	1·4893	1·5002	1·5195
Metaxylene*........	C_8H_{10}........	22·5	0·8641	1·4876	—	1·5079	1·5277
Paraxylene*	„	23·7	0·8602	1·4854	—	1·5058	1·5258
Orthoxylene*	„	24·1	0·8758	1·4928	—	1·5129	1·5328
Cinnamene	C_8H_8	21·0	0·9111	1·5318	1·5446	1·5615	1·5936
„ 2nd spec.*	„	21·4	0·9179	1·5336	—	1·5645	1·5973
„ after standing	„	25·0	0·9223	1·5333	—	1·5635	1·5957
„ „	„	26·4	0·9214	1·5330	—	1·5629	1·5957
„ „	„	30·0	0·9192	1·5303	—	1·5608	1·5928
„ „	„	33·0	0·9161	1·5293	—	1·5593	1·5917
β-Butenylbenzene,*	$C_{10}H_{12}$	21·0	0·9008	1·5269	1·5390	1·5545	1·5834
Diamylene*	$C_{10}H_{20}$	17·6	0·7710	1·4327	—	1·4445	1·4554
Cedrene	$C_{15}H_{24}$	13·0	0·942	1·5011	—	1·5133	1·5258
Carbon tetrachloride	CCl_4........	10·5	1·6058	1·4604	1·4661	1·4729	1·4843
„ „	„	12·0	1·598	1·4616	1·4674	—	1·4868

Substance.	Formula.	Temp. C.	Density.	μ_A.	μ_D.	μ_F.	μ_H.
Carbon tetrachloride	„	19·5°	1·586	1·4599	—	1·4733	1·4851
„ „ *	„	12·3	1·6095	1·4599	1·4656	1·4726	1·4835
„ dichloride	C_2Cl_4	12·5	1·6232	1·5006	1·5087	—	1·5359
Chloroform	$CHCl_3$	12·5	1·50245	1·4453	1·4506	1·4570	1·4677
Bromoform*	$CHBr_3$	19·0	2·891	1·5875	1·5980	1·6107	1·6334
Methyl iodide*	CH_3I	21·0	2·274	1·5185	1·5293	1·5423	1·5652
Methylene diiodide*	CH_2I_2	10·5	3·344	1·7275	1·7559	1·7750	1·8229?
Acetylene bromide	$C_2H_2Br_2$	20·0	2·256	1·5332	1·5428	—	1·5751
Ethylene bromide*	$C_2H_4Br_2$	10·5	2·2008	1·5361	1·5446	—	1·5722
Ethyl bromide*	C_2H_5Br	8·0	1·487	1·4263	1·4320	—	1·4503
Ethyl iodide*	C_2H_5I	7·0	1·9671	1·5124	1·5222	1·5343	1·5551
Allyl tribromide*	$C_3H_5Br_3$	7·0	2·4277	1·5824	1·5912	—	1·6205
Trimethylene iodide*	$C_3H_6I_2$	7·5	2·589	1·6347	1·6479	1·6643	1·6940
Isobutyl iodide*	C_4H_9I	7·0	1·6296	1·4958	1·5036	1·5140	1·5312
Glycerin	$C_3H_8O_3$	15·7	1·2594	1·4673	—	1·4778	1·4866
Chlorofumaric chloride*	$C_4HCl_3O_2$	25·7	1·5692	1·5088	1·5185	—	1·5556
Allylacetic acid*	$C_5H_8O_2$	7·5	0·9903	1·4283	1·4341	—	1·4522
Amyl formate	$C_6H_{12}O_2$	11·5	0·8832	1·3910	1·3951	1·4000	1·4084
Diallylacetic acid*	$C_8H_{12}O_2$	7·0	0·9618	1·4513	1·4574	—	1·4776
Ethyl acetyltrimethylenecarboxylate	$C_8H_{12}O_3$	25·2	1·0425	1·4383	1·4441	—	1·4629
Ethyl maleate*	$C_8H_{12}O_4$	7·5	1·0806	1·4405	1·4465	—	1·4659
Ethyl fumarate*	$C_8H_{12}O_4$	7·5	1·0693	1·4404	1·4471	—	1·4694
Ethyl chlorofumarate*	$C_8H_{11}ClO_4$	24·0	1·19517	1·4531	1·4598	—	1·4831
Ethyl acetyltetramethylenecarboxylate*	$C_9H_{14}O_3$	24·5	1·0605	1·7469	1·4772	—	1·5033
Safrole	$C_{10}H_{10}O_2$	11·3	1·0963	1·5286	1·5390	1·5524	1·5769
„	$C_{10}H_{10}O_2$	23·3	1·0813	1·5212	1·5314	—	1·5679
Orthoallylanisoïl*	$C_{10}H_{12}O$	20·0	0·9932	1·5467	1·5604	—	1·6154
Isoamyl oxide*	$C_{10}H_{22}O$	11·8	0·7826	1·4076	—	1·4169	1·4258
α-Parabutenylanisoïl*	$C_{11}H_{14}O$	19·0	0·9797	1·5426	1·5559	1·5733	1·6093
β-Parabutenylanisoïl*	„	23·0	0·9796	1·5360	1·5487	—	1·5976
Trimethylene cyanide*	$(CH_2)_3(CN)_2$	23·2	0·9888	1·4318	1·4365	1·4420	1·4514
Diethylamine*	$(C_2H_5)_2NH$	22·0	0·7050	1·3805	—	1·3906	1·3993
Triethylamine*	$(C_2H_5)_3N$	21·2	0·7280	1·3961	—	1·4067	1·4165
Propylamine*	$C_3H_7NH_2$	23·5	0·7140	1·3827	1·3873	1·3927	1·4011
„ *	„	6·5	0·7329	1·3922	—	1·4022	1·4111
Dipropylamine*	$(C_3H_7)_2NH$	23·2	0·7356	1·3983	—	1·4083	1·4172
„ *	„	4·4	0·753	1·4086	—	1·4191	1·4281
Tripropylamine*	$(C_3H_7)_3N$	22·8	0·7535	1·4121	1·4171	1·4229	1·4326
„ *	„	4·4	0·7703	1·4197	—	1·4306	1·4408
Propionitrile*	C_3H_5N	24·0	0·7816	1·3619	1·3659	1·3701	1·3778
Methyldiphenylamine*	$(C_6H_5)_2CNH_3$	24·6	1·0466	1·5998	1·6166	1·6391	1·6774
Benzylaniline*	$C_{13}H_{13}N$	24·8	1·0619	1·5974	1·6118	1·6301	1·6663?
„	„	26·3	1·0609	1·5967	1·6111	1·6297	1·6660?
Methyl sulphate*	$(CH_3)_2SO_4$	20·0	1·3269	1·3843	—	1·3921	1·3984
Ethyl thiocyanate*	C_2H_5SCN	20·0	1·0099	1·4593	—	1·4732	1·4864
Ethylthiocarbimide*	„	16·5	1·0030	1·5055	—	1·5279	1·5493
Stannic ethide	$(C_2H_5)_4Sn$	—	1·4089	1·5065	1·5143	—	1·5403
Zincic ethide	$(C_2H_5)_2Zn$	8·0	1·245	1·4936	—	1·5141	1·5336

From the foregoing data the molecular refraction can be calculated by dividing the index, minus unity, by the density, and multiplying by the molecular weight, $\frac{\mu - 1}{d}P$. The molecular dispersion is the difference between the molecular refraction of the lines A and H, or more shortly, $\frac{\mu_H - \mu_A}{d}P$. The theoretical values for the molecular refraction of any compound may be arrived at by adding together the recognised atomic refractions of the constituent elements; and the molecular dispersion can be reckoned on the same principle.

The following table contains the atomic refraction and dispersion of the elements with which we are concerned in this paper:—*

Substance.	At. wt.	R_A.	$R_H - R_A$.
Carbon	12	5·0	0·26
„ double linked	„	6·1	0·51 or 0 66
Hydrogen	1	1·3	0 04
Chlorine, with compound radicles	35·5	9·9	0·45
„ in olefines, &c.	„	10 0	0·50
Bromine, with compound radicles	80	15·3	1·03
„ in olefines, &c.	„	15·2	1·22
Iodine, with compound radicles	127	24·5	2·60
„ in olefines, &c.	„	25·35	3 65
Oxygen, double bond	16	3·4	0·18
„ single bonds	„	2·8	0·10
Sulphur, double bond	32	16·0	2·6
„ single bonds	„	14·1	1 2
Nitrogen, in nitriles	14	4·1	0 10
„ in bases	„	5·1	0·38
Tin	118	18·6?	—
Zinc	65	9·8	—

In the following table (next page) are given the experimental and the theoretical values for the molecular refraction and dispersion of the carbon compounds.

A glance at this table will show that in the case of pentane and most of the other substances the experimental and the theoretical numbers are in fairly close accordance in respect of both the optical properties. In some cases, however, there is an evident discrepancy; and it may be noticed that where a marked discrepancy occurs between

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* The actual figures are taken from my paper on "Refraction Equivalents" (*American Journal of Science*, 29, 55), and on "Dispersion Equivalents" (*Proc. Roy. Soc*, 1887, 42, 401), and from Messrs. J. H. and G. Gladstone's paper on "Fluorobenzene, and other Allied Compounds" (*Phil. Mag.*, 1891, 31, 1). At present these must be taken as only approximative, pending a full revision of the subject, which I hope shortly to be in a position to undertake.

Substance.	Formula.	Experimental.		Theoretical.	
		Molr. refrn.	Molr. dispn.	Molr. refrn.	Molr. dispn.
Pentane	C_5H_{12}	40·80	1·83	40·6	1·78
Heptane	C_7H_{16}	56·20	2·48	55·8	2·46
Do.	"	56·19	2 42	"	"
Do.	"	56·29	2·44	"	"
Amylene	C_5H_{10}	40·24	2·24	40 2	2·20
Benzene	C_6H_6	43·59	3·81	44·4	4·20
Toluene	C_7H_8	51·55	4·25	52·0	4·54
Metaxylene	C_8H_{10}	59·81	4·92	59·6	4·88
Paraxylene	"	59 80	4·93	"	"
Orthoxylene	"	59·64	4·85	"	"
Cinnamene	C_8H_8	60·70	7·06	59·2	5·6
Do. 2nd specimen	"	60·46	7·22	"	"
Do. after standing	"	60·10	7·06	"	"
β-Butenylbenzene	$C_{10}H_{12}$	77·20	8·23	74·4	6·28
Diamylene	$C_{10}H_{20}$	78·57	4·12	78·2	3·90
Cedrene	$C_{15}H_{24}$	108·52	5·35	108·4	5·36
Carbon tetrachloride	CCl_4	44·15	2·30	45 0	2·26
Do.	"	44·48	2·43	"	"
Do.	"	44·66	2·44	"	"
Do.	"	44·00	2·26	"	"
Carbon dichloride	C_2Cl_4	51·20	3·60	52·2	3·32
Chloroform	$CHCl_3$	35·42	1·78	36·3	1·80
Bromoform	$CHBr_3$	51·41	4·02	51·9	3·96
Methyl iodide	CH_3I	32·37	2·92	33·4	2·98
Methylene diiodide	CH_2I_2	58·30	7·65?	58·3	7·64
Acetylene bromide	$C_2H_2Br_2$	43·95	3·46	45·2	3·54
Ethylene bromide	$C_2H_4Br_2$	45·80	3·08	45·6	3·12
Ethyl bromide	C_2H_5Br	31·25	1·76	31·8	1·75
Ethyl iodide	C_2H_5I	40·64	3·38	41·0	3·32
Allyl tribromide	$C_3H_5Br_3$	67·41	4·41	67·1	4·64
Trimethylene iodide	$C_3H_6I_2$	72·57	6·77	71·8	6·22
Isobutyl iodide	C_4H_9I	55·98	4·00	56·2	4·00
Glycerin	$C_3H_8O_3$	34·14	1·41	33·8	1·40
Chlorofumaric chloride	$C_4HCl_3O_2$	60·80	5·59	61·6	4·31
Allylacetic acid	$C_5H_8O_2$	43·25	2·41	43 8	2·40
Amyl formate	$C_6H_{12}O_2$	51·35	2·29	51·8	2·32
Diallyacetic acid	$C_8H_{12}O_2$	65·69	3·83	66·2	3·84
Ethyl acetyltrimethylenecarboxylate	$C_8H_{12}O_3$	65·59	3·68	65·2	3·02
Ethyl maleate	$C_8H_{12}O_4$	70·11	4·04	70·2	3·92
Ethyl fumarate	"	70·85	4·66	72·4	4·72
Ethyl chlorofumarate	$C_8H_{11}ClO_4$	78·29	5·18	81 0	5·13
Ethyl acetyltetramethylenecarboxylate	$C_9H_{14}O_3$	75·29	5·39	—	—
Safrole	$C_{10}H_{10}O_2$	78·11	7·14	78·0	6·48
Do.	$C_{10}H_{10}O_2$	78·09	6·99	78·0	6·48
Orthoallylanisoïl	$C_{10}H_{12}O$	81·46	10·24	—	—
Isoamyl oxide	$C_{10}H_{22}O$	82·29	3·68	81·4	3·58
α-Parabutenylanisoïl	$C_{11}H_{14}O$	89·71	11 09	—	—
β-Parabutenylanisoïl	"	88·65	10·17	—	—
Trimethylene cyanide	$(CH_2)_3(CN)_2$	41·05	1·85	41·0	1·74
Diethylamine	$(C_2H_5)_2NH$	39·40	1·95	39·4	1·86
Triethylamine	$(C_2H_5)_3N$	54·95	2·88	54·6	2·54

Substance.	Formula.	Experimental.		Theoretical.	
		Molr. refrn.	Molr. dispn.	Molr. refrn.	Molr. dispn.
Propylamine	$C_3H_7NH_2$	31·62	1·52	31·8	1·52
Do.	„	31·57	1·52	„	„
Dipropylamine	$(C_3H_7)_2NH$	54·69	2·59	54·6	2·54
Do.	„	54·80	2·62	„	„
Tripropylamine	$(C_3H_7)_3N$	78·21	3·89	77·4	3·56
Do.	„	77·91	3·92	„	„
Propionitrile	C_3H_5N	25·47	1·12	25·6	1·08
Methyldiphenylamine ..	$(C_6H_5)_2CNH_3$	104·88	13·56	100·2	9·08
Benzylaniline	$C_{13}H_{13}N$	102·94	11·92	„	„
Methyl sulphate	$(CH_3)_2SO_4$	36·49	1·34	—	—
Ethyl thiocyanate	C_2H_5SCN	39·57	2·33	39·7	2·28
Ethylthiocarbimide ..	„	43·85	3·80	43·8	4·18
Stannic ethide	$(C_2H_5)_4Sn$	84·12	5·54	84·6	—
Zincic ethide	$(C_2H_5)_2Zn$	48·88	3·97	42·8	—

theory and experiment in the refraction, a still greater proportionate discrepancy frequently occurs in the dispersion.

The following points in regard to some of the substances may be worthy of notice:—

Heptane.—The substance examined was Professor Thorpe's specimen derived from *Pinus sabiniana,* which has good claims to be considered as specially pure. It will be observed that the molecular refraction is about 0·4 higher than that calculated from theory. This suggests the idea that CH_2 is not exactly 7·6, as usually assumed, but about midway between that number and 7·7. From a general comparison of the data existing in 1884, I was led to assign to it the value of 7·63 (Trans., 1884, **45**, 251). The theoretical molecular dispersion coincides well with the experimental.

Amylene.—The addition made for the one pair of double-linked carbons in the dispersion is the lower figure 0·5*, as in the allyl compounds.

Benzene.—This specimen was made from benzoic acid. Its molecular refraction and dispersion agree with those determined from specimens prepared in the ordinary way. They are both decidedly less than the figures calculated from the general run of aromatic compounds.

Toluene.—The same remarks apply, but the discrepancy is only about half as great. These peculiarities of benzene and toluene are commented upon, so far as refraction is concerned, in my paper on

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* That is, the difference between 0·26 (the atomic dispersion for ordinary carbon) and 0·51 (the lower value for a double-linked carbon atom) twice over.

"Refraction Equivalents" (Trans., 1884, **45**, 253). I am not yet able to find any explanation.

Xylenes.—The three xylenes agree very closely in molecular refraction and dispersion, the considerable difference in their indices being compensated by corresponding differences in their densities. The orthoxylene is practically identical with the theoretical values; and the others, unlike the previous members of the series, are not lower, but even a trifle higher than theory.

Cinnamene and Butenylbenzene.—In these two cases, in which there are four pairs of double-linked carbons, the experimental values are decidedly higher than the theoretical. They may be added to the substances referred to in my paper (*Proc. Roy. Soc.*, **31**, 329), in which I ventured to assign a still higher value than 6·1 to a carbon atom, which "has all four of its units of atomicity satisfied by other carbon atoms, each of which has the higher value of 6 0 or 6·1."

Cedrene.—The specimen examined was prepared with great care. It indicates only one pair of double-linked carbon atoms, which is more probable than the constitution formerly ascribed to the essential oils of the $C_{15}H_{24}$ group. I hope to revert to this subject on some future occasion.

HALOGEN COMPOUNDS.—With these there will be found a general agreement between experiment and theory; but it ought to be stated that several of the observations recorded in this table were used among other data for determining the values of chlorine, bromine, and iodine in different states of combination. Nevertheless, I doubt it these values have been exactly estimated as yet; at any rate, there seem to be discrepancies. Thus the experimental values for tetrachloride of carbon and for chloroform given in the table are in good accordance with previous determinations of the same substances, and they indicate a dispersion equivalent for chlorine of at least 0·50, but a refraction equivalent of from 9·7 to 9·9 instead of 10·0.

Carbon Dichloride and Acetylene Bromide.—In both of these substances we should expect a double linking, and though the numbers do not agree very well, both optical properties point in that direction.

OXYGEN COMPOUNDS.—The compounds containing oxygen present some peculiarities worthy of notice. There are three cases of isomerides differing in their optical properties; and some bodies of extremely high refraction.

Ethyl Maleate and Fumarate.—The optical properties of ethyl maleate answer very well to what may be expected of a substance having the composition of $C_8H_{12}O_4$ with one double linking, which gives in the dispersion the higher value of 0·8. Ethyl fumarate, on the contrary, indicates rather two double linkings, both giving the additional value of 0·8 in the dispersion. The molecular magnetic rotation, according to Perkin, is also higher in the fumarate than the maleate. There are, however, a chlorine substitution product of ethyl fumarate, and another of fumaric acid, which do not altogether bear out this view.

Safrole.—This oil was prepared in my laboratory. The optical properties are fairly accordant with the formula $CH_2{<}\substack{O\\O}{>}C_6H_3{\cdot}C_3H_5$, the substance containing a phenyl nucleus with its three double linkings, and another pair of double-linked carbons in the side-chain. It differs from anethol in not requiring us to suppose the existence of any carbon of a still higher refraction than 6·1.

Allylacetic Acid and Diallylacetic Acid.—These two are interesting, as they agree perfectly with one another, and with the theory that has been for some time established for allyl compounds, viz., that 2·2 is to be added to the molecular refraction, and 0·5 to the molecular dispersion, for each unsaturated C_3H_5.

The Anise Oils.—These are all so high that they indicate the extreme value for one of the carbons which has been already referred to under the head of cinnamene. The orthoallylanisoïl of Perkin is the same as what is generally called anethol, and agrees with former determinations. The two isomeric parabutenylanisoïls appear to differ in optical properties.

NITROGEN COMPOUNDS.—The compounds of nitrogen in the list, whether they are nitriles or cyanides, all give refraction and dispersion equivalents so nearly coincident with theory as to leave no doubt that the optical properties confirm the chemical views of their composition. The following points also are worthy of notice:—

Propylamines.—Beneath the determinations of the three specimens at a low temperature are placed those of the same specimens made on a very hot day, though the latter have been already published. They show that the difference of 17° or 18° makes so little difference in the molecular refraction or dispersion that it is not to be distinguished from the ordinary error of experiment.

Methyldiphenylamine and Benzylaniline.—This pair of isomeric bodies differ in their optical properties, and both appear to be above what would be theoretically required; but aniline itself, according to several observers, has a higher refraction and dispersion than might be expected, and one which would almost exactly account for the experimental figures for benzylaniline. The methyldiphenylamine has still higher optical properties.

Ethyl Thiocyanate and Ethylthiocarbimide.—The first of these isomerides gives results quite in accordance with the chemical view of its constitution. The figures are similar to those obtained by

Nasini. The second gives much higher values, which, however, agree closely with the isothiocyanate of Nasini, and a previous determination of my own. They indicate that the sulphur is united by two bonds, which necessitates also a double linking of the carbons.

Stannic Ethide.—This confirms fairly the value formerly assigned for the refraction of tin from the determinations of its tetrachloride. The dispersion of tin has not yet been given; but if it is calculated from the tetrachloride (*Phil. Trans.*, 1869, 28) it will be 2·42, whilst stannic ethide will give 2·66. The *zincic ethide*, on the contrary, differs widely from what might be expected from the refraction of zinc salts in solution. The specimen was prepared in my laboratory, and the refraction agrees substantially with that deduced from Bleekrode's observation. The values of the two metals as determined from these ethides would be—

Tin ...... $R_A = 18·1$ .... $R_H - R_A = 2·66$
Zinc ...... $R_A = 15·9$ .... $R_H - R_A = 2·53$

Halogen Compounds.

In addition to the halogen compounds contained in the preceding list, there occur in my note books the following, which do not contain carbon :—

Substance.	Formula.	Temp. C.	Density.	μ_A.	μ_D.	μ_F.	μ_H.
Silicon tetrachloride....	$SiCl_4$ ...	10·5°	1·504	1·4156	1·4207	—	1·4360
,, ,, ...	,,	14·0	1·4987	1·4139	—	1·4248	1·4334
Silicon tetrabromide....	$SiBr_4$ ...	15·5	2·7906	1·5586	—	1·5794	1·5988
Titanium tetrachloride..	$TiCl_4$ ...	10·5	1·744	1·5928	1·6112	—	—
,, ,, ..	,,	—	1·7228	1 5851	1·6039	1·6296	1·6814

The figures give the following molecular values :—

Substance.	Formula.	R_A.	$R_H - R_A$.
Silicon tetrachloride........................	$SiCl_4$....	47·11	2·32
,, ,, ...	,, ...	47·09	2·22
Silicon tetrabromide........................	$SiBr_4$	69·76	5·02
Titanium tetrachloride........................	$TiCl_4$	65·26	—
,, ,, ...	,, ...	65·20	10·74

Silicon Tetrachloride.—These two observations, made from different specimens, not only agree remarkably well with one another, but also with the value published by Haagen as far back as 1867, from whose

Substance.	Formula.	Temp. C.	Density	μ_A	μ_B.	μ_C.	μ_D.	μ_F.	μ_G	μ_H.
Benzene	C_6H_6	7·5°	0·8881	1·4972	—	1·5021	1·5070	1·5189	—	1·5402
Toluene.....................	C_7H_8	7·5	0·8701	1·4895	—	1·4941	1·4982	1·5097	—	1·5297
Caoutchene..................	$C_{10}H_{16}$	17·2	0·8396	1·4665	—	1·4700	1·4733	1·4818	—	1·4963
Naphthalene monobromide......	$C_{10}H_7Br$........	17·5	1·5403	1·6463	—	1·6553	1·6638	1·6879	—	1·7300
Cinnamic alcohol	$C_9H_{10}O$	13·0	1·0318	1·5465	—	1·5525	1·5579	1·5734	—	1·6022
α-Methyl orthoxyphenylate of methyl	$C_{11}H_{12}O_3$........	10·5	1·1412	1·5570	1·5617	—	1·5717	1·5929	1·6213	1·6419
β-Methyl orthoxyphenylate of methyl	„	10·0	1·1527	1·5720	1·5781	—	1·5904	1·6175	1·6553	1·6818
Aniline.....................	C_6H_7N.........	7·5	1·0322	1·5780	—	1·5847	1·5921	1·6102	—	1·6449
Methyl diphenylamine..	$CH_3N(C_6H_5)_2$...	24·6	1·0466	1·5998	—	1·6083	1·6166	1·6391	1·6634	1·6774
Carbon bisulphide............	CS_2...........	16·0	1·2706	1·6116	—	1·6213	1·6308	1·6556	—	1·7032

numbers R_α would be calculated at 47·06, and $R_\gamma - R_\alpha$ at 1·428, which is about equivalent to 2·27 for $R_H - R_A$. From this the refraction equivalent of silicon, 7·4 was deduced. Assuming that chlorine in the tetrachlorides has the same value as in the organic olefine compounds, Mr. George Gladstone and I, in our paper on Fluorides (*loc. cit.*), estimated the refraction equivalent of silicon at 7·07, and the dispersion equivalent at 0·32. These figures are not well supported by the specimen of tetrabromide of silicon, for which I am indebted to Professor Thorpe. The refraction equivalent calculated from it on similar principles would be as much as 9 6, and the dispersion equivalent only 0·14.

Titanium Tetrachloride.—The two specimens agree well. An early experiment of mine, published in 1869, gave R_A as 65·08, and indicated a similar length of spectrum. The refraction does not differ widely from an observation made by H. Becquerel. Reckoning as in the case of the carbon and silicon compounds, titanium would appear to have a refraction equivalent of 25·2, and the enormous dispersion equivalent of about 8·7.

Additional Lines of the Spectrum.

My notes frequently contain observations of lines in the spectrum, other than A, D, F, and H, more particularly in those substances that have a high dispersive power. As these may be interesting in some inquiries, the more important ones are subjoined, whether the substances have been given already in this or in previous papers.

I hope, with the permission of the Society, shortly to give a further communication dealing with various observations upon the refraction and dispersion of substances in solution.

XXXIII.—*Citraconfluorescein.*

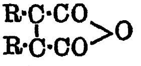
By J. T. Hewitt, B.A., B.Sc., Assoc. R.C.S.

I. *Theoretical.*

The three acids, citraconic, itaconic, and mesaconic, have been worked at by many chemists, with a view to the settlement of their constitution. In the similar case of fumaric and maleic acids, a satisfactory explanation has been given, assigning to the former a formula indicating axial, whilst the latter is taken to exhibit plane, symmetry. This hypothesis is well borne out by the inability of the former acid to form an anhydride (Liapin, *J. Russ. Chem. Soc.*, 13, 140), whilst maleïc acid readily yields such a compound on distillation, water being eliminated. In addition to this, there is the transformation of maleïc into fumaric acid by the action of small amounts of hydriodic or hydrobromic acids, a rotation of the two halves of the molecule relatively to one another taking place.

The isomerism exhibited by citraconic and mesaconic acids is explained similarly on the Van't Hoff hypothesis (*Dix Années*, p. 79), citraconic acid being the methyl derivative of maleïc acid, whilst mesaconic holds the same relationship to fumaric acid. But we have the case complicated by the presence of the third isomeride, itaconic acid, which also easily yields an anhydride, and is formed from citraconic acid by simple reactions. If citraconic anhydride is heated for some hours with water at 150°, itaconic acid is produced (Wilm, *Annalen*, 141, 28), but if citraconic acid is treated with hydrochloric, hydrobromic, or hydriodic acid, mesaconic acid is formed. On the other hand, although itaconic anhydride distils unchanged under a pressure of 30 mm., yet at the ordinary pressure it is converted into citraconic anhydride.

Again, all the three acids give the same methylsuccinic acid, $CH_3\cdot CH(COOH)\cdot CH_2\cdot COOH$, on reduction with sodium amalgam. Hence, although mesaconic acid may be well regarded as the methyl derivative of fumaric acid, yet the relationships of itaconic and citraconic acids are not so apparent. Again, in the case of acids with the formula $C(CH_3)(COOH){:}C(CH_3)\cdot COOH$, we are acquainted with pyrocinchonic acid only, which, although it does not exist in the free state, but only in its anhydride and salts, has nevertheless been generally regarded as dimethylfumaric acid. In order to prove that citraconic acid and pyrocinchonic acid are true homologues of maleic acid, it would be as well if in some particular instance we could show that their anhydrides behave in a precisely similar manner.

Lunge and Burckhardt have found that a maleïnfluoresceïn is formed when 1 mol. of maleïc anhydride and 2 mols. of resorcinol are heated together for two hours (*Ber.*, 17, 1598); this I consider to be a typical reaction, since only anhydrides of the type  $\left.\begin{array}{l}R\cdot C\cdot CO\\ \;\;\;|\\ R\cdot C\cdot CO\end{array}\right>O$ condense in this way (*e.g.*, maleïc, phthalic, and substituted phthalic anhydrides); and have succeeded in applying it to citraconic anhydride, with formation of a fluorescent derivative.

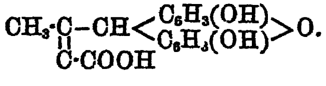
II. *Practical.*

Citraconfluoresceïn.—Although citraconic anhydride and resorcinol form a condensation product when heated together, the addition of a small quantity of sulphuric acid makes the reaction take place much more readily; I therefore adopted the following method of preparation:—10 grams of citraconic anhydride and 20 grams of resorcin were melted together, with the addition of 5 grams of concentrated sulphuric acid. After fusion, a uniform mixture was obtained, which was heated on a water-bath for about half an hour. On cooling, the dark-red product was first partially purified by washing it with cold water, until no traces of sulphuric acid could be detected in the washings; by this means any excess of citraconic anhydride or resorcinol was also removed, the citraconfluoresceïn being only sparingly soluble in cold water. The residue was then extracted with dilute alcohol, in which the citraconfluoresceïn readily dissolved with a brown colour and green fluorescence, not so vivid, however, as that shown by ordinary fluorescein. The alcohol was then allowed to evaporate slowly at the temperature of the laboratory, but no crystals were deposited; on drying the residue in a vacuum over sulphuric acid, a fine red, vitreous, transparent mass was obtained, which was finely powdered, and further dried for some days over strong sulphuric acid. Analysis of this compound showed that it contained 4 mols. H_2O.

0·1696 gram gave 0·3451 gram CO_2, and 0·0811 gram H_2O.

	Calculated for $C_{17}H_{12}O_5,4H_2O$.	Found.
C	55·43	55·44
H	5·43	5·31

Citraconfluoresceïn is readily soluble in alcohol and in glacial acetic acid, fairly soluble in water, forming a yellowish-brown solution having a green fluorescence lighter in colour than that possessed by the alcoholic solution; it is somewhat soluble in benzene, but only sparingly in ether yielding a yellow solution; it is practically insoluble in toluene, even on boiling. The addition of sodium chloride causes the separation of citraconfluoresceïn from its aqueous solution. In alkalis, the substance dissolves with a magnificent purple colour by transmitted light, the solution exhibiting a dark-green fluorescence; but the ammoniacal solution loses this colour on boiling, the ammonia being expelled. The solution in caustic soda is decolorised on allowing it to stand in contact with zinc filings, but the colour is restored by weak oxidising agents, such as potassium ferricyanide; from this it follows that the carbinol group alone is reduced, and that the double is not converted into a single linkage, a citraconfluorescin being obtained, probably of the formula



$$\begin{array}{l}CH_3\cdot C-CH<\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}>O.\\ \qquad\ \ \| \\ \qquad\ \ C\cdot COOH\end{array}$$

Citraconfluorescein melts at 70—75° (uncorr.), and appears to decompose at 109°, this, however, is probably only due to an evolution of water vapour.

The tetrahydrated compound, dried at 100°, loses 2 mols. H_2O, giving $C_{17}H_{12}O_5,2H_2O$. Analysis gave the following result:—

0·1678 gram gave 0·3792 gram CO_2, and 0·0795 gram H_2O.

	Theory for $C_{17}H_{12}O_5,2H_2O$.	Found.
C	61·45	61·63
H	4·83	5·26

Calcium Salt.—If citraconfluorescein is boiled for some time with water and calcium carbonate, some of the latter dissolves; on filtering off the excess of calcium carbonate and allowing the solution to cool, minute spheroids of a calcium salt separate out. but if the solution be at once evaporated on the water-bath, the salt is obtained as a fine, orange-coloured, transparent, amorphous mass, easily soluble in water yielding a yellow solution with a bright green fluorescence. Calcium estimations agree with the formula $C_{17}H_{10}O_5Ca,8H_2O$.

I. 0·1506 gram gave 0·0424 gram $CaSO_4$.
II. 0·0319 gram gave 0·0319 gram $CaSO_4$.

	Calculated for $C_{17}H_{10}O_5Ca,8H_2O$.	Found. I.	Found. II.
Ca	8·37	8·21	8·45

If in the preparation of the calcium salt a mixture of the carbonate and hydroxide is used instead of the former alone, a dark purple solution is obtained, and on evaporation purple crusts of a basic salt separate, 0·2162 gram of which yielded 0·1198 gram $CaSO_4$, corresponding to 16·29 per cent. of calcium.

Silver Salt.—On adding silver nitrate solution to the solution of the yellow calcium salt, a bright yellow, flocculent precipitate is thrown down, but decomposes almost immediately, darkening considerably, even before it can be filtered, thus preventing a silver estimation of this compound.

Lead Salts.—When lead acetate solution is added to a solution of the yellow calcium salt, an orange, flocculent precipitate is thrown down, but the solution is not completely decolorised, owing to the somewhat soluble nature of the lead derivative. On filtering off the precipitate and drying it at 100°, lead citraconfluoresceinate is obtained as a light, brick-red, amorphous powder, a lead estimation of which showed it to be $C_{17}H_{10}O_5Pb$.

0 1692 gram gave 0·0794 gram PbO.

	Theory for $C_{17}H_{10}O_5Pb$.	Found.
Pb	41·32	41·61

If, however, the lead acetate contains some free acetic acid, a lighter yellow precipitate is obtained, which becomes bright orange on drying. The amount of lead contained in this is smaller.

0 1089 gram yielded 0·0417 gram $PbSO_4$.

	Calculated for $(C_{17}H_{11}O_5)_2Pb$.	Found
Pb	25 97	26 16

Both the above salts are sufficiently soluble in water for the solutions, after filtration from the corresponding salts, to give a voluminous, splendid, purple precipitate on the addition of ammonia. This precipitate was digested for some time with neutral lead acetate solution, in order to remove any precipitated lead hydroxide as basic lead acetate, then filtered off and dried first on the filter pump, and then at 100°.

0 2962 gram gave 0·2812 gram $PbSO_4$.

	Calculated for $C_{17}H_{10}O_5Pb,2PbO$.	Found
Pb	65·58	65·97

This basic compound forms a fine, dark-purple, amorphous powder, insoluble in water.

I have obtained nitro- and bromo-derivatives of citraconfluorescein, the former being dark-brown, and the latter a pale-pink substance, the alcoholic solution of which is a fine red. These I have not yet fully worked out, but hope shortly to lay further details before the Society.

University Laboratory,
Cambridge.

XXXIV.—*The Oxidation of Mannitol by Nitric Acid. d.-Mannosaccharic Acid.*

By T. H. Easterfield, B.A. (Junior Demonstrator in the University
Laboratory, Cambridge).

According to the text-books on organic chemistry, saccharic acid may be obtained by oxidising mannitol with nitric acid. This statement appears to date as far back as 1860, when Backhaus (*Neu. Rep. Pharm.*, 9, 291, &c.; *Jahresber.*, 1861, 522) announced that he had obtained oxalic and a small quantity of saccharic acid by oxidising mannitol with nitric acid according to the method given by Liebig (*Jahresber.*, 1860) for the oxidation of milk-sugar to tartaric acid.

A close relationship should, therefore, exist between mannitol and saccharic acid, and this conclusion seemed to be further strengthened by the observation that dextrose yields mannitol when reduced with sodium amalgam, but yields saccharic acid when oxidised by nitric acid.

The recent researches of Emil Fischer and his pupils have, however, shown that dextrose on reduction yields mannitol with difficulty, whereas mannose, the stereochemical isomeride of dextrose, passes almost quantitatively into mannitol when treated with sodium amalgam. This result seemed to indicate that the relationship between dextrose and mannitol was not so simple as had been supposed. The close relationship between mannitol and mannose, however, is shown by the ease with which the one can be converted into the other. If mannose be further oxidised with bromine-water, it yields monobasic d.-mannonic acid, which may be oxidised by nitric acid to bibasic d.-mannosaccharic acid, isomeric with ordinary saccharic acid (Wirthle, *Dissertation, Erlangen*, 1890). The new acid differs markedly from saccharic acid, more especially in that it yields no sparingly soluble acid potassium salt, and passes readily by internal condensation into a crystalline double lactone.

These results made it appear probable that mannitol would not yield saccharic by direct oxidation with nitric acid, but mannosaccharic acid; and at Professor Fischer's suggestion, I have carried out the oxidation with nitric acid of various strengths. Our supposition as to the nature of the reaction was completely realised, mannosaccharic and oxalic acids being the only products which could be identified.

In the first place, in order to ascertain whether saccharic acid was formed by the oxidation of mannitol, 5 grams of mannitol were warmed on the water-bath with 30 grams of nitric acid of sp. gr. 1·15;

when the reaction had almost ceased, the liquid was evaporated to a syrup, diluted with water, and again evaporated, so as to get rid of excess of nitric and nitrous acids and to destroy any nitro-compounds which might be present. The syrup was then diluted with 30 c.c. of water, exactly neutralised with potassium carbonate, evaporated to a small bulk, and an excess of acetic acid added. No crystallisation occurred even when crystals of acid potassium saccharate were placed in the liquid and allowed to remain there for several days. Saccharic acid cannot, therefore, have been produced in the reaction. A like result was arrived at when experiments were made on a larger scale and with more highly concentrated nitric acid.

The next step was to find out what acid, if any, had been produced in the above operation. With this object, 10 grams of mannitol were oxidised as above described, and the syrup, after having been diluted to 250—300 c.c., was boiled with precipitated chalk until neutral to test-paper. The liquid was filtered, a considerable quantity of calcium oxalate together with unaltered chalk remaining on the filter. The dark-brown filtrate, after being evaporated until a film appeared on its surface, was allowed to cool, when a reddish-brown calcium salt separated. This to the naked eye appeared crystalline, but under the microscope was found to consist of aggregates of most characteristic nodules, bearing an astonishing likeness to a yeast plant. A further quantity of the salt was precipitated on adding alcohol to the mother liquor.

Although this calcium salt is not remarkably insoluble in water, it is somewhat difficult to get into solution, for if put into hot water it melts to a thick oil which remains at the bottom of the liquid, darkens in colour, and then passes into solution very slowly indeed. If, however, the crude calcium salt be ground to a very thin paste with cold water, and then added gradually to a large quantity of boiling water, it dissolves immediately, giving a darkly coloured solution which can be readily decolorised with animal charcoal. On concentrating the solution, the calcium salt separates out on cooling as a cream-coloured powder which under the microscope exhibits the same structure as the crude salt. If the solution is allowed to evaporate spontaneously, the salt separates out in vitreous grains with no well-developed faces. These grains have no action on polarised light.

The calcium salt contains water and is efflorescent; after drying at 100°, it gave the following result:—

0·1880 gram gave 0·1035 gram $CaSO_4$.

	Found.	Calculated for $C_6H_8O_8Ca$.
Ca	16·19	16·12

The salt would thus appear to be calcium saccharate or an isomer thereof. That it was not ordinary calcium saccharate was proved by decomposing 1 gram of the salt with an equivalent amount of potassium carbonate, concentrating, and adding acetic acid. No sparingly soluble salt separated out.

A silver salt was prepared from the concentrated solution of the calcium salt. It could not be recrystallised, and rapidly darkened in colour. Upon analysis,

I. 0·1646 gram gave 0·0978 gram CO_2, 0·0305 gram H_2O, and 0·0813 gram Ag.

II. 0·1691 gram gave 0·1009 gram CO_2, 0·0378 gram H_2O, and 0·0835 gram Ag.

	Found.		Calculated for
	I.	II.	$C_6H_8O_8Ag_2,H_2O$.
C	16·20	16·26	16·28
H	2·05	2·48	2·26
Ag........	49·39	49·37	48·86

These results could not be regarded as satisfactory, and it was decided to attempt the preparation of the free acid from the calcium salt by decomposition with oxalic acid. In the meantime, the above results were communicated to Professor Emil Fischer, who kindly forwarded a specimen of the lactone of d.-mannosaccharic acid for comparison with the acid which I was about to prepare.

On decomposing the calcium salt with an equivalent quantity of oxalic acid, filtering, and concentrating, a syrup was obtained which refused to crystallise even after long standing. The addition of a crystal of Fischer's lactone, however, immediately caused the syrup to change to a solid mass of crystals These were freed as completely as possible from mother liquor by means of a vacuum filter, washed with ice-cold water, and then recrystallised from hot water. The substance was thus obtained in colourless needles, which, after washing with absolute alcohol, gave the following results on analysis :—

0·1407 gram gave 0·0593 gram H_2O and 0·1750 gram CO_2.

	Found.	Calculated for $C_6H_{10}O_8$.
C..............	33·91	34·28
H.......... ...	4·68	4·76

These results agree with those to be expected from an acid, and not from a lactone; the crystals, however, effloresce, and by drying in a vacuum over sulphuric acid lose 2 mols. H_2O.

Of the dried substance,

0·1308 gram gave 0·0393 gram H_2O and 0·1977 gram CO_2.

	Found.	Calculated for $C_6H_6O_6$.
C..............	41·21	41·37
H.............	3·33	3·44

The colourless, efflorescent crystals above mentioned would seem to be merely the lactone crystallised with 2 mols. H_2O, and not the acid itself; for if these crystals are dissolved in water, the solution is absolutely neutral when freshly prepared. After standing, however, for some hours, the solution acquires an acid taste and reddens litmus strongly, showing that the lactone passes into the acid when in solution. The identity of the above lactone with Fischer's d.-mannosaccharolactone appears to be complete. The fact that the latter crystallises in the first instance with 2 mols. H_2O is, indeed, not mentioned in Wirthle's dissertation, but it is a fact which might well escape notice. The points of resemblance are the following:—

(1.) The two lactones (both dried over sulphuric acid) when placed in capillary tubes, and heated side by side in a sulphuric acid bath, exhibited exactly the same behaviour. At 170°, they began to darken, and at 182°, both melted with decomposition.

(2.) A small quantity of Fischer's lactone, when boiled with chalk and the filtered solution concentrated, yielded a calcium salt which separated in microscopic spherules, just like those furnished by the calcium salt from mannitol.

(3.) Both reduce Fehling's solution strongly; this, however, is a character shared by many other oxy-acids.

(4.) Both are strongly dextrorotatory. Mr. H. E. Schmitz, of St. John's College, has kindly made some experiments upon the optical properties of the lactone. Unfortunately, I had left Cambridge, and was unable to supply him with sufficient material to finish his investigations. Suffice it to say that in a solution, the strength of which was only about 1 per cent., the apparent sp. rot. power $[\alpha]_D = +167·9°$. That of d.-mannosaccharolactone in 5 per cent. solution $= +197·1°$. I hope to be enabled to communicate an accurate determination of the rotatory power in a subsequent note.

It remains to discuss the best method for the preparation of the lactone from mannitol. Hitherto the best yield has been obtained as follows:—

20 grams of mannitol are placed in a small flask, and covered with 120 grams of nitric acid, sp. gr. 1·15, and the flask slowly warmed in a water-bath, a thermometer being placed inside the flask. When the contents of the flask have obtained a temperature of 75°, the thermometer begins to rise rapidly, showing that an energetic action is begin-

ning. The flask is now cooled down to 65°, and kept between 65° and 70° until the reaction has nearly ceased; generally 5—6 hours. The temperature is now allowed to rise slowly to 80°, and after the reaction has again diminished, the flask is kept at 90° for a couple of hours.

If the contents of the flask be now diluted with water, boiled with an excess of chalk, and filtered, a solution will be obtained which, when evaporated to saturation, and poured into five times its volume of alcohol, deposits the whole of the calcium salt as an amorphous, flocculent precipitate. If this is washed by decantation, then well shaken up with water, and the turbid liquid poured into a large volume of boiling water, the salt goes completely into solution. The solution, after being decolorised with animal charcoal, yields the calcium salt as a nearly colourless powder. By this method, 80 grams of mannitol yielded 32 grams of crude calcium salt, and this, after recrystallisation, gave 20 grams of pure salt, that is, 25 per cent. of the mannitol employed.

The acid may, however, be prepared from the crude oxidation product without first preparing the calcium salt; for this purpose, the product of the oxidation is evaporated in an open dish, with constant stirring, until a syrup is produced. This, if slightly diluted and allowed to cool, deposits a large quantity of oxalic acid, which must be filtered off and the mother liquor concentrated. On now adding a crystal of the lactone (prepared from the calcium salt) to the solution, the product will solidify, and can be purified by recrystallisation from water. Sometimes the liquid crystallises of its own accord, but usually refuses obstinately to do so; the addition of alcohol assists the crystallisation.

10 grams of mannitol treated in this manner gave 0·9 gram of pure lactone, but I have little doubt that the process can be modified so as to give a better yield.

XXXV.—*Studies of the Terpenes and allied compounds. The nature of Turpentine oils, including that obtained from* Pinus Khasyana.

By Henry E. Armstrong.

Among the compounds which attracted my attention when I began to study terpenes and allied compounds, now many years ago, was the crystalline substance of the formula $C_{10}H_{18}O_2$, briefly described by Sobrero, in 1851 (*Compt. rend.*, **33**, 66; *Annalen*, **80**, 106), obtained by exposing oil of turpentine together with moist oxygen to sunlight —a substance which was rendered none the less interesting by Sobrero's statement that, when boiled with dilute sulphuric acid, it was converted into a volatile product having a strong odour resembling that of camphor as well as that of turpentine.

It was to be supposed that Sobrero had worked with French oil of turpentine, and therefore this was first submitted to air-oxidation in sunlight; the results obtained were in complete accordance with the account given by Sobrero. On substituting American for French turpentine, a substance was obtained identical with that resulting from the oxidation of the French hydrocarbon, except in its optical characters.

These results led me to study the behaviour of oils from various sources containing $C_{10}H_{16}$ hydrocarbons, in the hope that information might be gained which would serve to elucidate the complex problem presented by the existence of an apparently infinite variety of essential oils.

It was soon ascertained that a clear atmosphere and a bright, high sun—conditions which are always exceptional in London—were requisite for the formation of the crystals. It has rarely happened that crystals began to form until late in May, and each exposure has usually lasted from two to three months. Necessarily, therefore, the information has been acquired at a slow rate. The earlier experiments were carried on at the London Institution, Finsbury Circus, on the roof—a particularly unsuitable locality. But very little progress was made during the subsequent years in which the arrangement of the laboratory and the organisation of the teaching, first at the Finsbury Technical College, and very shortly afterwards at the Central Institution, claimed my attention. During the past three summers, the experiments have been regularly resumed at the Central Institution, and it has been possible, chiefly owing to the important assistance which one of my students, Mr. Pope, has rendered me in submitting the products to crystallographic examination, to collate the scattered results.

The conclusions arrived at are, I venture to think, of some importance, and justify the hope formed at an early period of the enquiry, that a comparative study of the air-oxidation products from various oils would not be without interest.

The following passage from the second edition of my *Introduction to the Study of Organic Chemistry* (London: Longmans, Green, & Co.), published in 1880, is here quoted as an indication of the views which guided me in the enquiry, and which are justified in the present note:—

"The hydrocarbons of the formula $C_{10}H_{16}$, derived from plants, may be divided into two classes, viz., (1) those boiling at about 156°, which are conveniently termed *terpenes*, as they are the chief constituents of ordinary turpentine oils; and (2) those boiling at about 176—178°, which may be termed *citrenes*, as they are the chief constituents of the oils derived from the various species of *Citrus*. The terpenes and citrenes are all capable of rotating the plane of polarisation of light, but no two plants furnish terpenes or citrenes of identical rotatory power, and often different parts of the same plant yield different products; the different terpenes appear, however, to agree in all other physical properties, and also in their chemical properties; and the same is true of the different citrenes. It is probable that the number of isomerides of the formula $C_{10}H_{16}$ is very much smaller than has been supposed, and that the differences observed in the rotatory powers of the hydrocarbons from various sources are due to their being mixtures in varying proportions of two or more isomerides" (p. 106).

In a paper read before the Society of Chemical Industry, in 1882 (their Journal, p. 478), detailing the results of the examination of a very large number of samples, representing many thousand barrels of different kinds of commercial turpentine, after calling attention to the almost absolute uniformity of the French oil and the wide variation which was noticeable on comparing the rotatory powers of different samples of the American oil, I stated that I had been led to think it not unlikely that the low dextrorotatory power of American turpentine is due "to the presence of a lævorotatory turpentine; this would serve to explain the difference in optical character of products from different localities." That this is actually the case I have no longer any doubt. The crystalline product from French turpentine is all but uniform; that from American turpentine is but rarely so: the earlier crystallisations usually consist of a substance which may be said to be the image of that from the French oil, but although the crystals in later fractions may exhibit the same melting point as those separated at an early stage, the rotatory power of the fraction as a whole is lower. The explanation of the difference was discovered in the course of the examination of a very beautiful turpentine oil from British Burmah, the produce of *Pinus Khasyana*, which came into my possession in 1881, through the kind assistance of Mr. Thiselton Dyer, the Director of the Royal Gardens, Kew. This oil is in every respect, so far as I have been able to ascertain, the counterpart of French turpentine, but its optical image, and if it could be obtained in quantity would form a most valuable article of commerce; a description of its derivatives will form the subject of a later communication. The air-oxidation product of the Khasyana terpene is the image of that from French turpentine and identical with that obtained from American oil, the difference in the Burmese and American oils being that the former, like the French oil, affords a more nearly uniform product.

When the two varieties of equal opposite rotatory power of the oxidation product are mixed, an inactive substance is obtained of much lower melting point, and it is this substance which is present in considerable quantity in the product from American oil along with the dextrorotatory active form. The melting point observed in the case of the later fractions of the product from American turpentine is a matter of accident, for if the crystal used in the determination be not specially selected from the mass, it may be either the active or the inactive substance.

As the relation of the crystalline oxidation product to the parent hydrocarbon cannot yet be determined, and as it is not improbable that, as in other cases, a molecular change has attended its formation, and that it is not a simple derivative of the hydrocarbon, I would suggest that in giving it a name (as one or both of its oxygen atoms possess alcoholic functions), to recognise its discovery by Sobrero, it be termed *sobrerol*.

The numerous observations which I have made lead me to think that sobrerol is only obtainable from the terpenes proper; and that, according as an oil yields either dextro- or lævo-sobrerol, or a mixture of either modification with the inactive form, it is to be regarded as containing one or other of the corresponding terpenes, or, as in the case of American turpentine, a mixture of the two. In other words, *that there are but two terpenes*, viz., those represented by the essential components of the French and Burmese oils.

Bearing in mind that we are indebted to Berthelot for the first systematic study of the varieties of turpentine oil, and that he proposed the name *terebenthene* for the characteristic hydrocarbon of such oils, as a matter of justice, it would appear but right to retain this name, terming the two optically different varieties *dextroterebenthene* and *lævoterebenthene*.

So long as we are unaware of the structure of the terebenthenes, it is impossible to pronounce an opinion on theoretical grounds as to the possibility or otherwise of a distinct inactive modification; the argument from analogy alone makes the existence of such an intra-compensated modification conceivable, however.

The oil which Sobrero obtained by distilling the crystalline oxidation product with acid has proved to be identical with the isomeride of camphor, which Wallach and Otto obtained by the interaction of turpentine and nitrous acid (*Annalen*, **253**, 249), which they have named *pinol*. Being a strict adherent to the view that the *ol* termination should be reserved for hydroxy-derivatives exhibiting alcoholic functions, as the compound does not appear to be of this class, I have ventured to suggest (Proc., 1890, 99) that it should be named *sobrerone*, to indicate its relationship to sobrerol. Having succeeded in reconverting "pinol" into the crystalline oxidation product, $C_{10}H_{18}O_2$, Wallach (*Annalen*, **259**, 313) proposes to name the latter *pinol hydrate*; unfortunately this name also appears to me to be inappropriate, for the reason that it is desirable to restrict the term hydrate, as far as possible, to compounds containing so-called water of crystallisation.

The "sobrerone" obtained from the two active modifications of sobrerol is optically inactive, and when reconverted into sobrerol by Wallach's method, yields the inactive form of the latter.

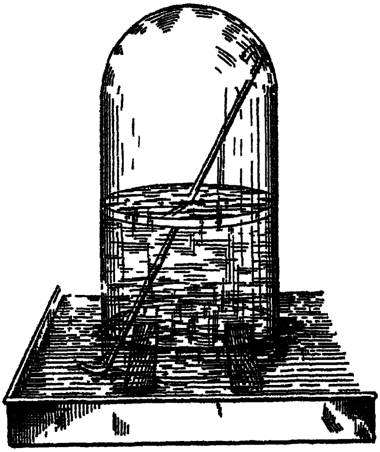
It is to be mentioned that the proportion of crystalline oxidation product obtained is relatively very small, the greater part of the turpentine being converted into the well known non-volatile viscid oil. Much better results would be obtained, I imagine, if the oxidation were effected under the influence of a tropical sun. As it appeared possible that the viscid oil might contain some sobrerol, it was digested with dilute sulphuric acid and steam-distilled; a considerable amount of volatile oil was obtained, but hitherto all attempts to separate "sobrerone" from this have failed. Notwithstanding that the greater part of the hydrocarbon is converted into products other than sobrerol, as dextro- and lævo-terebenthene are apparently oxidisable at the same rate under similar conditions, it is to be supposed that when a mixture is oxidised the crystalline product will regularly betray its origin, unless, indeed, pressure have a perceptible influence on the rate of oxidation. On oxidising American turpentine fractionally, that is to say, if, when the oxidation has gone on for some time, the crystals are collected and the unoxidised oil is separated by steam-distilling and re-exposed to oxidation, &c., a series of products are obtained, the first of which has a higher dextrorotatory power than subsequent fractions. This is exactly what should happen if dextroterebenthene be the chief constituent of American turpentine.

It appears not unlikely that sobrerol may occur naturally; I have, however, only on one occasion met with evidence of its presence. In the course of the investigation of so-called terebene which Professor Tilden and I carried out several years ago, I had occasion to distil a large quantity of American turpentine which I had received in a wooden barrel. The most volatile portion was collected separately, and put away in a blue Winchester quart, in a dark cellar; after a time, the sides and bottom of the bottle were found to be encrusted with crystals, which were collected and recrystallised from alcohol. Only a very few grams of the crystals were thus obtained from 10 gallons of turpentine. This substance has proved to be *inactive* sobrerol, chiefly mixed with some dextrosobrerol.

XXXVI.—*Studies of the Terpenes and allied compounds. Sobrerol, a product of the oxidation of Terebenthene (Oil of Turpentine) in Sunlight.*

By Henry E. Armstrong and W. J. Pope.

Preparation of Sobrerol.—The most convenient form of vessel in which to effect the oxidation of turpentine in sunlight is the common glass statuette shade, a suitable size being that about 6 inches in diameter and 14 inches high. A number of these shades are ranged side by side in a wooden, zinc-lined tray about 2 inches deep; they are placed across two laths three-eighths of an inch thick, so that a glass tube, bent as shown in the following figure (p. 316), may rest within the shade with the one end projecting beneath the edge of the shade into the water outside. The tray being full of water, the shade with the tube inside is placed across the laths, and an indiarubber tube having been attached to the outside end of the glass tube, air is sucked out until the water has risen within the shade and fills about one-third of it; the rubber tube is then detached, and 50—100 c.c. of turpentine delivered from a pipette underneath the edge of the shade. As the oxygen of the air is gradually absorbed, the water rises and crystals begin to collect on the interior after three or four days' exposure in bright sunshine. Oxygen, to replace that absorbed, is run in whenever necessary by attaching a rubber tube, connected with an oxygen reservoir, to the lower end of the glass tube in the shade. When a clearly defined crystalline deposit has formed over the shade down to the "nitrogen line," *i.e.*, the level to which the water rises when all oxygen is absorbed from the air, the shade may be filled with oxygen down to the level of the water in the tray, as the formation of crystals becomes confined to the upper part of the shade. The greatest speed of absorption noticed has been that indicated by a rise of the water 2 inches per day, but this has occurred only in abnormally bright weather with an atmosphere rich in oxygen. After six weeks' exposure or so, the oil begins to sink; the shades are then removed with the aid of a large clock glass, set aside to drain for a few hours, and the lower part cleaned with the aid of spirit; the crystalline deposit is then scraped out as far as possible by means of a flexible steel spatula, the undetached portion being removed by rinsing with hot spirit.



To purify the crude product, it is dissolved in a minimum quantity of boiling alcohol, the solution digested with animal charcoal, filtered, and rapidly cooled; by continually stirring, the crystals are caused to separate in the form of a fine meal, from which the liquor is easily expressed on a vacuum filter. If necessary, this operation is repeated, and, finally, the substance is allowed to crystallise out slowly from alcohol.

The following results, obtained on combustion of the substance so prepared, serve to verify the formula originally assigned to the product by Sobrero:—

	Experiment.		Calculated.
Carbon per cent.......	70·57	70·49	70·57
Hydrogen per cent.....	10 71	10·74	10·61

Dextro- and Lævo-sobrerol.

The pure substance melts at 150°. In a solution, in ordinary spirit, containing 5 grams per 100 c.c., it exhibits the specific rotatory power, $[\alpha]_D = \pm 150°$. We do not claim any high degree of accuracy for this value, and propose to redetermine it when we are satisfied that we are dealing with a substance of undoubted purity.

Active sobrerol separates from its alcoholic solution in the form of long, tabular crystals attaining a length of 30 mm., and from water as stout prisms. The two isomerides, as might be expected, crystallise in enantiomorphous hemihedral forms. The crystals possess a vitreous lustre, and are colourless and transparent.

The following are the crystallographic data which establish the form of sobrerol (Fig. 1):—

Angle.	Number of observations.	Limits.	Mean.	Calculated.
ac	34	83° 14′—83° 58′	83° 38′	—
am	11	67 5—67 31	67 21	—
pc	7	43 5—44 14	43 41	—
ap	5	79 15—79 30	79 27	79° 8′
cm	12	87 11—87 43	87 33	87 33½′

Crystalline system. Monosymmetric.

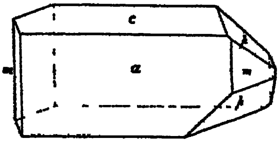
$$a : b : c = 2{\cdot}4113 : 1 : 0{\cdot}8531.$$

$$\beta = 83° \, 38'.$$

Forms present.

a .... $\{100\}$ .... $\infty\bar{P}\infty$
c . .. $\{001\}$ .... $0P$
m .... $\{110\}$ .... ∞P
p .... $\{\bar{1}11\}$ .... $+P$.

FIG. 1.



The crystals exhibit a perfect cleavage parallel to the ortho-pinakoid (100), and an imperfect one parallel to the basal plane (001). The double refraction is negative and strong. The optic axial plane is nearly parallel to the basal plane, and the acute bisectrix is nearly perpendicular to the ortho-pinakoid; the axial angle is very large.

The crystals are flexible, and may be readily bent backwards and forwards several times, the cleavage surfaces sliding upon each other. They are extremely soft, and may be easily rubbed into cleavage splinters between the fingers.

In very rare instances the hemihedrism is shown by the suppression of one-half of the pyramid (İĪ1) faces. The crystals nearly always consist of the forms *a*, *c*, and *m* alone, the hemihedral character being shown by an internal skeletal structure, which gives rise to a wedge-shaped inclusion, pointing towards opposite ends of the prism in the two oppositely active modifications (see Figs. 2 and 3). The direction of the rotation in solution may be very readily determined by means of this structure. Placing the crystal with the form (100) facing the observer, and with the obtuse axial angle in front and at the upper part of the crystal, so that the basal plane is visible as in the figures, in the case of a crystal of the lævosobrerol, the skeletal structure points from right to left, while if the crystal be one of dextrosobrerol, the wedge points from left to right.

FIG. 2.

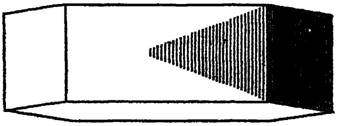
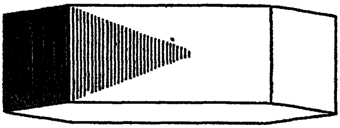


FIG. 3.



One of the ortho-pinakoid faces is very brilliant, the parallel one being more or less tesselated in character; the form (001) is very perfect, no distinction being noticeable between the parallel faces; contiguous faces of the form (110) are generally dull, while the parallel ones are almost wholly destroyed by the skeletal structure; the pyramid faces appear but seldom, and only upon crystals which do not show the above described skeletal structure, and which have all the faces of each form similar in character. The pyramid faces are large, but much rounded, and the measurements, which are obtained with difficulty, cannot be relied upon as accurate.

Twinning.—One crystal was found in which (100) was the twin plane and face of composition.

Inactive Sobrerol.

This substance is at once obtained on allowing a solution of equal weights of the two active modifications to crystallise. It melts at 130·5—131°. The crystals are totally different in appearance from those of the active forms, and never exhibit the peculiar internal structure which characterise the latter. The following data serve to determine the crystallographic constants :—

Angle.	Number of observations.	Limits	Mean	Calculated
am	19	66° 16′—68° 53′	67° 35′	—
ad	17	70 7—72 36	71 10	—
dm	8	82 50—83 5	82 56	82° 55′

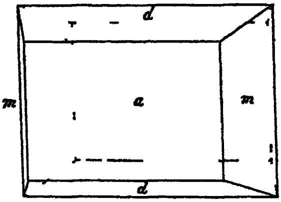
Crystalline system Orthorhombic.

$a : b : c = 2{\cdot}4242 : 1 : 0{\cdot}8268.$

Forms present.

a .... {100} .... $\infty\breve{P}\infty$
m .... {110} .... ∞P
d .... {101} .... $\breve{P}\infty$.

FIG. 4.



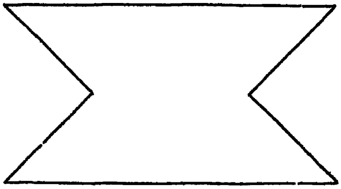
As crystallised from alcohol, the substance consists of flat, colourless, transparent tables, with bevelled edges (Fig 4); they exhibit slight vitreous lustre, and a perfect cleavage parallel to (100), and an imperfect fibrous cleavage parallel to (001).

The optic axial plane is parallel to (001), and the axes emerge nearly normal to (110) The acute axial angle is therefore nearly 44° 50′.

The double refraction is strong and negative.

When a drop of the alcoholic solution is evaporated on a microscope slide, a large proportion of the small crystals so obtained present under the microscope the peculiar form shown in the figure (Fig 5), which much resembles a skeletal structure like that possessed by the active modification, but symmetrically developed; measurable crystals do not generally show the structure, but one

FIG. 5.



crystal has been obtained showing such a double skeletal structure in a well-developed state, extending from both ends of the crystal, and meeting in an hour-glass form at the centre.

The crystals may be crushed between the fingers into long, fibrous cleavage fragments. The inactive crystals are far more brittle than those of the active modification, and the cleavage laminæ do not slide over one another in so striking a manner as in the monosymmetric crystals.

Active and inactive sobrerol possess considerable crystallographic interest on account of their extraordinarily close similarity to each other, a similarity much greater than that which generally subsists between the active and inactive modification of a compound. It will be seen from the description that in their axial ratios, their habit, their optical orientation, the position of their optic axes, the sign and magnitude of double refraction, and their cleavages they are practically identical. The only differences in dimensions are that the angle β is 90° for the inactive and 83° 38′ for the active modification, and that the forms developed are different.

The resemblance even extends to the skeletal structure described above, with the important differences that this structure is unsymmetrical or wedge-shaped for the active, but symmetrical or hour-glass shaped for the inactive, modification.

The preparation of optical sections was found impossible, owing to the softness and flexibility of the crystals.

In conclusion, we desire to express our thanks to Mr. Miers, Instructor in Crystallography in the Central Institution, for the assistance and advice which he has most kindly given to one of us (W. J. P.) in carrying out the crystallographic study of sobrerol.

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Exhibition Road, London.

XXXVII.—*A Rapid Method of Estimating Nitrates in Potable Waters.*

By George Harrow, Ph.D., F.I C.

The usual method of estimating nitrates in potable waters, the mercury method of Crum, as modified by Frankland and Armstrong, though yielding accurate results, requires a very considerable time for its performance. It frequently happens that an analyst desires to form an opinion as to the purity of a water in a short space of time, and so far as the estimations of ammonia and "albumenoïd" ammonia, examination by means of the Forchammer process, and estimation of chlorine are concerned, results are easily and rapidly obtained; it is only the determination of nitrogen as nitrates and nitrites that materially prolongs the analysis, so that a process which would give the nitrogen as nitrates and nitrites as accurately as the mercury process and as rapidly as the determination of ammonia by Nessler's test appears to be wanted.

The method which I have devised for this purpose is founded on Griess' extremely sensitive nitrite test (α-naphthylamine and sulphanilic acid), and depends on the conversion of nitric acid into nitrous acid by means of zinc-dust; that this conversion is a partial one, and that other products, ammonia and hydroxylamine, are formed, does not affect the delicacy of the test or the accuracy of the determination.

The test solution used consists of

α-Naphthylamine	1 gram.
Sulphanilic acid....................	1 "
Ordinary strong hydrochloric acid	25 c.c.

dissolved in about 200 c.c. of distilled water, boiled with a small quantity of animal charcoal, filtered, and made up to 500 c.c.

Standard solutions containing

1·0 part N as nitrates per 100,000.
0·1 " " "
0·01 " " "

To prepare these solutions, 0·721 gram of pure and dry potassium nitrate is dissolved in 1 litre of water; the resulting solution contains 10·0 parts of N per 100,000, and may be readily diluted to the strength required. If many water analyses are to be made, it is as well to make up a Winchester quart of each of the standards.

A small quantity of zinc-dust is also required, contained in a wide-mouthed bottle, into the cork of which a miniature spatula, constructed of brass or platinum foil, should be fixed.

The process is conducted as follows:—50 c.c. of each water to be tested, and as many as four estimations may readily be conducted at the same time, are placed in beakers (100 c.c. contents) side by side on a sheet of white paper, and with them, in three similar beakers, 50 c.c. of each of the standard nitrate solutions; to each beaker is now added 10 c.c. of the test solution,* and afterwards a very small quantity of zinc-dust (7 to 8 milligrams) by means of the miniature spatula; the quantity added should be approximately the same in each case, and I find that there is no difficulty in effecting this. If nitrates be present in the waters, a more or less intense pink colour will make its appearance, and this colour may be compared with that produced in the three standard nitrate solutions, after the lapse of 15 minutes; a rough approximation to the truth is obtained in this first experiment.

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* If *nitrites* are present the pink colour will, of course, appear without the addition of zinc-dust; Griess' test.

To get an accurate result, the water must be diluted until the colour produced is very nearly like that given by one of the standards; perhaps the greatest accuracy may be obtained with the most dilute standard, and, if it be used, a hundredfold dilution of the water to be tested is frequently advisable; the necessary dilution is, of course, indicated by the first experiment.

The diluted waters are again tested against standards 0·1 or 0·01, and, after 15 minutes, the colours carefully compared in Nesslerising cylinders of equal calibre, which may be conveniently graduated at the side. The standard solution occupying 60 c.c. in one cylinder, the water tested is run into the other until the depth of colour appears to be equal; a reading is then made of the quantity necessary, say, 45 c.c. were employed. Then 45 : 60 :: 0·1 : x (= 0·133), and

Water.	Dilution of water.	Nitrogen as nitrates and nitrites; parts per 100,000.		Absence or presence of *traces* of nitrite in the water examined.
		New test.	Mercury method.	
1	1 in 100	5·32	5·00	Nitrites absent.
"	"	5·3	"	
"	"	5·4	"	
2	1 in 10	3·16	3·00	Nitrites present.
"	1 in 25	3·25	"	
3	1 in 10	2·86	2 6	Nitrites absent.
4	undiluted	1·60	1·44	Nitrites present.
"	1 in 50	1·70	"	
5	undiluted	1·20	1·35	Nitrites present.
"	1 in 10	1·20	"	
"	1 in 50	1·07	"	
6	1 in 10	1·00	1·06	Nitrites absent.
7	1 in 5	0·58	0·61	Nitrites absent.
8	undiluted	0·58	0·56	Nitrites present.
"	1 in 10	0·67	"	
"	1 in 25	0·55	"	
9	1 in 5	0 50	0·49	Nitrites absent.
10	undiluted	0·13	0·12	Nitrites absent.
"	"	0·12	"	
11	undiluted	0·03	absent	Nitrites absent.

supposing the water to have been 10 times diluted it would contain 1·33 parts nitrogen as nitrates and nitrites.

The advantages of the process are its rapidity, simplicity, and ease of execution, and the small quantity of water required for analysis. 20 c.c. is sufficient for the purpose, and enables one to make several determinations.

The only precaution necessary, so far as I have observed, is to avoid the addition of large quantities of zinc-dust, which would decolorise the solution.

The results of nitrogen determinations in various waters by means of the method above described, as compared with the results obtained by the mercury process, are contained in the table (p. 322).

XXXVIII.—*Some Compounds of Dextrose with the Oxides of Nickel, Chromium, and Iron.*

By Alfred C. Chapman.

In a previous communication to the Society (Trans., 1889, 55, 576), I described a compound of dextrose with oxide of zinc, prepared by adding a solution of zinc hydrate in aqueous ammonia to a concentrated solution of dextrose in 90 per cent. alcohol. It occurred to me that a similar compound of dextrose with oxide of nickel might be obtained by substituting hydrate of nickel for hydrate of zinc in the above method.

Nickel Dextrosate.

If washed hydrate of nickel is dissolved in strong aqueous ammonia, and the solution added to a concentrated solution of dextrose in 90 per cent. alcohol, a pale-green precipitate falls. If the alcohol be weaker, precipitation will not occur at once, but only after standing for some time, and in any case is not complete until the lapse of one or two days. This green precipitate was collected on a filter, thoroughly washed with alcohol, and, after partial drying in the air, was dried to a constant weight in a vacuum over sulphuric acid.

Results of Analysis.

I. 0·2275 gram gave 0·156 gram CO_2 and 0·0935 gram H_2O.
II. 0·2500 „ 0·0975 gram NiO.
III. 0·2500 „ 0·0970 „
IV. 0·4000 „ 0·1540 „

	Calculated for	Found			
	$C_6H_{12}O_6,2NiO + 3H_2O$.	I	II.	III.	IV
C	18·79	18 68	—	—	—
H	4·69	4·39	—	—	—
Ni	30·54	—	30·62	30 47	30·25

The nickel dextrosate of the above composition is a pale-green, amorphous substance, insoluble in water and alcohol, but easily soluble in dilute acids. When boiled with water, it undergoes partial decomposition into dextrose and oxide of nickel, but it appears to be much more stable than the corresponding zinc compound. When heated, it commences to decompose at a temperature of about 100°, and on ignition leaves a residue of nickel oxide.

Chromium Dextrosate.

When a solution of chromic chloride is added gradually to a large excess of cold, strong aqueous ammonia, the precipitated hydrate partly redissolves, forming a more or less purple-coloured solution. If this liquid is added to a concentrated solution of dextrose in 90 per cent. alcohol, a lilac-coloured, flocculent precipitate falls.

As in the case of the nickel compound, the solution must be allowed to stand for a day or two, in order to ensure its complete separation. This substance was collected and thoroughly washed with alcohol. It was partially dried in the air, and then dried to a constant weight in a vacuum over sulphuric acid.

The analyses of different preparations of this substance showed that its composition varied with the conditions under which it was prepared, the strength of the alcoholic liquid after the addition of the chromium solution appearing to exercise the greatest influence.

Results of Analysis.

I. 0·184 gram gave 0·112 gram CO_2 and 0·081 gram H_2O.
II. 0·3165 „ 0·200 „ 0·148 „
III. 0·200 „ 0·077 gram Cr_2O_3.
IV. 0·0925 „ 0 036 „

	Calculated for	Found.			
	$C_6H_{12}O_6,Cr_2O_3 + 4H_2O$.	I.	II.	III.	IV.
C	17·77	16·63	17·25	—	—
H	4·93	4 89	5·17	—	—
Cr	25·92	—	—	26·42	26·70

The numbers obtained on submitting to analysis a mixture of six separate preparations are those given in Analysis II, and the various analytical results, though not so concordant as might have been expected, point to the above formula as representing, at least approximately, the composition of the compound in question.

If an excess of dextrose be dissolved in a strong aqueous solution of chromic chloride, the hydrate of chromium, which is at first precipitated on the addition of ammonia, redissolves almost completely on standing for a short time. If the resulting claret-coloured liquid, after filtering from any undissolved hydrate of chromium, is poured into a large excess of 90 per cent. alcohol, the flocculent chromium dextrosate is at once precipitated.

By this method the compound may be more readily prepared, and in larger quantity, than by that first described, since the solubility of the chromic hydrate is increased by the presence of the dextrose.

The following experiment was made in order to determine the effect of heat on the compound. 0·25 gram of the substance, dried as usual to a constant weight in a vacuum, was put into an air-bath at 80°. When the temperature had risen to 90° the compound had a green tinge, and when the temperature of 110° was reached, the originally slate-coloured substance had become sage-green. On drying at this temperature for some hours, the weight finally became constant at 0·206 gram, showing a loss of 17·6 per cent. On heating to a much higher temperature, the compound charred and underwent further decomposition.

The chromium dextrosate above referred to is a slate-coloured, amorphous substance insoluble in water and alcohol, but soluble in acids. In the moist condition, when freshly prepared, it dissolves readily in water, and on boiling this solution, the chromic hydrate is precipitated. On boiling the dried substance with water, it undergoes partial decomposition into dextrose and oxide of chromium, and on ignition, leaves a residue of chromic oxide. When heated, it burns with extreme readiness. If, for instance, some of the dry compound is placed in a small platinum dish, and momentary heat applied to one side of the dish, so as to heat only a small portion of the substance, incandescence spreads throughout the whole mass, leaving a black residue of the metallic oxide mixed with unburnt carbon.

Ferric Dextrosate.

When ammonia is added to a solution of ferric chloride in which an excess of dextrose has been dissolved, a reddish precipitate forms, which redissolves on standing, giving a deep-red solution. If the excess of dextrose be sufficiently large, and if the ammonia be added slowly, the formation of a precipitate may be altogether prevented. When the red liquid thus obtained is poured into a large excess of

90 per cent. alcohol, a red, flocculent precipitate immediately forms. This precipitate was collected, washed with alcohol, and dried to a constant weight in a vacuum as in the case of the other compounds.

Results of Analysis.

I. 0·495 gram gave 0·309 gram CO_2 and 0·162 gram H_2O.
II. 0·537 „ 0·326 „ 0·165 „
III. 0 250 „ 0·135 gram Fe_2O_3.
IV. 0·319 „ 0·174 „

	Calculated for	Found.			
	$2C_6H_{12}O_6,3Fe_2O_3 + 3H_2O$.	I.	II.	III.	IV.
C	16·10	16·95	16·55	—	—
H	3·35	3 63	3·40	—	—
Fe	37·58	—	—	37·71	38·11

The results obtained in the analysis of this compound point to slight variation in the composition of the various preparations, even when, to all appearance, precisely the same method was adopted. When the dried compound was heated in the air-bath at 80°, the colour changed from orange-red to dark-brown, and on heating for some hours at a temperature of 105°, it lost about 21 per cent. of its weight.

The ferric dextrosate whose composition is represented by the above formula is an orange-red, amorphous substance. It will not dissolve either in water or in alcohol, but when first prepared and while still moist, it dissolves easily in water, giving a deep-red solution. On boiling this solution, the iron is precipitated, leaving the liquid colourless. Ammonia produces no precipitate when added to an aqueous solution of the iron dextrosate. Ammonium sulphide, on the addition of the first drop, gives a brown coloration, and on adding more, the black sulphide of iron is formed. Potassic ferrocyanide and potassic thiocyanate produce no change, but if the compound be first decomposed by the addition of a few drops of hydrochloric acid, Prussian blue is at once obtained in the one case, and the red thiocyanate of iron in the other. On boiling the dried compound with water, it is partially decomposed, and on ignition, leaves a residue of ferric oxide.

When the dry substance is heated, incandescence spreads throughout the whole mass, just as in the case of the chromium compound before described.

XXXIX.—*Action of Acetic Acid on Phenylthiocarbimide.*

By J. C. Cain and J. B. Cohen, Ph.D., Owens College, Manchester.

One of us has shown (Trans., 1890, **57**, 67) that the product of the action of phenylthiocarbimide on benzoic acid is benzanilide, and not dibenzanilid as stated by Losanitsch. A similar reaction between phenylthiocarbimide and glacial acetic acid has been studied by Hofmann (*Ber.*, **3**, 770), who states that diacetanilide is produced with evolution of hydrogen sulphide and carbon dioxide, according to the following equation:—

$$C_6H_5{\cdot}NCS + 2C_2H_4O_2 = C_6H_5{\cdot}N(C_2H_3O)_2 + H_2S + CO_2.$$

This experiment was repeated by Claus and Völtzkow (*Ber.*, **14**, 445) and Gumpert (*J. pr. Chem.* [2], **32**, 294), who showed that acetanilide was the sole product formed. We have repeated Hofmann's experiment with the object of determining, if possible, the course of a reaction which might proceed in several stages, thus:

1. $2C_6H_5{\cdot}NCS + 4C_2H_4O_2 = (C_6H_5{\cdot}NH)_2CS + 2(C_2H_3O)_2O + H_2S + CO_2.$
2. $(C_6H_5{\cdot}NH)_2CS + 2C_2H_4O_2 = (C_6H_5{\cdot}NH)_2CO + (C_2H_3O)_2O + H_2S.$
3. $(C_6H_5{\cdot}NH)_2CO + 2C_2H_4O_2 = 2C_6H_5{\cdot}NH_2 + CO_2 + (C_2H_3O)_2O.$

The aniline formed in the last reaction would then be free to combine with acetic acid and thus yield acetanilide.

It is obvious that a similar series of products might be formed by the action of water alone, with aniline as the final product.

In order to prove whether the presence of small quantities of water in the acetic acid determined the direction of the reaction, we made two experiments according to Hofmann's method, using, however, in the one case, glacial acetic acid, distilled after standing over phosphorus pentoxide, and in the other, the ordinary strong acid. The amount of acetic acid taken was, in each case, slightly in excess of that calculated from the equation given by Hofmann.

A third experiment was made at a temperature of 170° instead of at 130—140°. The first two experiments gave results which were identical. Besides hydrogen sulphide and carbon dioxide, two solid products were formed, which were readily separated by their different solubilities in alcohol. The one crystallised in plates melting at 112°, and proved to be acetanilide; the second, of which a smaller quantity was present, crystallised in needles melting at 235°, and was diphenylcarbamide. An analysis of the latter gave the following result:—

0.1805 gram substance gave 20·2 c.c. N at 774·6 mm. and 16°.
N found 13·52 per cent.; calculated for $(C_6H_5{\cdot}NH)_2CO$, 13·21 per cent.

The solid products of this reaction were free from sulphur, and therefore diphenylthiocarbamide was not formed.

In the third experiment, acetanilide alone was produced. It appears, therefore, that the formation of diphenylcarbamide is dependent on the temperature. We proved this to be the case; for when the experiment was repeated at the temperature of the steam-bath, continuing the heating for several days, a much larger quantity of the needles and a comparatively smaller quantity of the plates of acetanilide were found in the tube.

A final determination conducted at a temperature of about 70° also yielded diphenylcarbamide.

As water may be one of the substances formed in the reaction, more especially in the last stage when acetanilide is produced, it appeared of some interest to study the action of water alone on phenylthiocarbimide. This reaction takes a somewhat different course, a fact which indicates that water plays, if any, a subordinate part in breaking down the molecule.

In the experiment which is here given, the evolution of hydrogen sulphide and carbon dioxide was accompanied by the formation of diphenylthiocarbamide.

5 grams of phenylthiocarbimide were heated with 1 gram of water in a sealed tube at 150° for $3\frac{1}{2}$ hours. The resulting crystalline mass was purified and found to contain sulphur. On comparing its melting point with that of diphenylthiocarbamide prepared from aniline and carbon bisulphide, the two compounds proved to be identical, both melting at 147·5°. The reaction takes place according to the following equation:—

$$2C_6H_5{\cdot}NCS + 2H_2O = (C_6H_5{\cdot}NH)_2CS + H_2S + CO_2.$$

When diphenylthiocarbamide is in its turn heated with water under pressure to a somewhat higher temperature, the product is aniline, the rate and extent of the reaction depending mainly on the temperature to which the mixture is heated. 5 grams of diphenylthiocarbamide were heated with an equal weight of water for 6—7 hours at 150°; but very little action took place. When, however, the temperature was raised to 170°, the whole of the thiocarbamide was converted into aniline, and hydrogen sulphide was evolved on opening the tube. When diphenylthiocarbamide is heated with an amount of water sufficient to combine with the sulphur alone under the above conditions, a portion only of the substance is converted into aniline, the remainder being unchanged.

When dilute acetic acid was substituted for water, aniline was also formed. In no case was the presence of diphenylcarbamide detected.

If, however, diphenylthiocarbamide be heated with glacial acetic acid, diphenylcarbamide is produced. 5 grams of the thiocarbamide were heated with about 1 gram of acetic acid, dehydrated over phosphorus pentoxide, at a temperature of 130—140° for 3—4 hours. On crystallising the product from alcohol, needles of diphenylcarbamide melting at 235° were obtained.

From the above experiments, it appears very probable that the changes which occur on heating together phenylthiocarbimide and acetic acid are independent of the presence of water, and take place in two stages according to the following equations:—

$$1.\ 2C_6H_5\cdot NCS + 6C_2H_4O_2 = (C_6H_5\cdot NH)_2CO + 3(C_2H_3O)_2O + 2H_2S + CO_2.$$

$$2.\ (C_6H_5\cdot NH)_2CO + 2C_2H_4O_2 = 2C_6H_5\cdot NH_2 + CO_2 + (C_2H_3O)_2O.$$

We are at present engaged in the study of the bi-acid derivatives of the aromatic bases, which appear not to have been prepared.

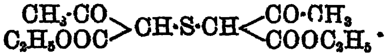
XL.—*Ethyl Thiacetoacetate.*

By Charles T. Sprague, B.Sc., Ph.D.

Ethyl thiacetoacetate was discovered by the late Professor Hubner, of Göttingen, when investigating the action of chloride of sulphur on the sodium salt of ethyl acetoacetate. His death occurring shortly after this discovery, the investigation was continued by Buchka (*Ber.*, 18, 209), who found that, in this reaction, a substance $C_{12}H_{18}O_6S$ was formed, along with sodium chloride and sulphur:—

$$2CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5 + S_2Cl_2 = C_{12}H_{18}O_6S + S + 2NaCl.$$

Buchka named this substance "acetoacetic estersulphide," and proposed the following constitution for it:—

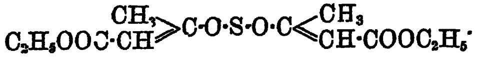


$$\begin{matrix}CH_3\cdot CO\\C_2H_5OOC\end{matrix}\!\!>CH\cdot S\cdot CH<\!\!\begin{matrix}CO\cdot CH_3\\COOC_2H_5\end{matrix}.$$

Later on Deliole (*Ber.*, **20**, 2008) obtained the same substance by treating ethyl acetoacetate with sulphur dichloride, as follows:—

$$2C_6H_{10}O_3 + SCl_2 = C_{12}H_{18}O_6S + 2HCl.$$

Since he, like Buchka, found that it evolved hydrogen sulphide on treatment with reducing agents, he proposed for it the constitution



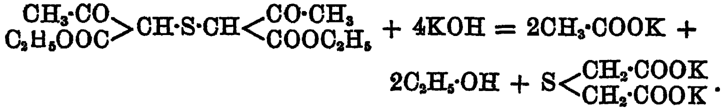
$$\left.\begin{matrix}CH_3\\C_2H_5OOC\cdot CH\end{matrix}\right>C\cdot O\cdot S\cdot O\cdot C\left<\begin{matrix}CH_3\\CH\cdot COOC_2H_5\end{matrix}\right.$$

The object of my research was to study the properties and reactions of this compound, and. if possible, to decide between the above constitutional formulæ. During my investigations, Schönbrodt published an account of a research (*Annalen*, **253**, 168), in the course of which he obtained ethyl thiacetoacetate by the action of sulphur on the copper salt of ethyl acetoacetate in benzene solution, as follows:—

$$C_{12}H_{18}O_6Cu + S_2 = C_{12}H_{18}O_6S + CuS.$$

Schönbrodt confirmed the empirical formula $C_{12}H_{18}O_6S$, and attempted to prove the constitution of the substance.

According to him, on saponifying ethyl thiacetoacetate with caustic potash, thiodiglycollic acid is formed in the following manner:—



$$\left.\begin{matrix}CH_3\cdot CO\\C_2H_5OOC\end{matrix}\right>CH\cdot S\cdot CH\left<\begin{matrix}CO\cdot CH_3\\COOC_2H_5\end{matrix}\right. + 4KOH = 2CH_3\cdot COOK + 2C_2H_5\cdot OH + S\left<\begin{matrix}CH_2\cdot COOK\\CH_2\cdot COOK\end{matrix}\right..$$

The above reaction seems to be a decisive proof of the constitution of the compound, but, unfortunately, on a careful repetition of Schönbrodt's experiment, I was only able to obtain a minute trace of substance quite insufficient for analysis. Buchka and Pampel (*Ber.*, **22**, 2546) obtained the sodium salt of ethyl thiacetoacetate by acting on an ethereal solution of it with sodium. This salt has the composition $C_{12}H_{16}O_6SNa_2$, a proof that two acid hydrogen atoms are contained in the molecule of ethyl thiacetoacetate. Recently Michaelis and Phillips (*Ber.*, **23**, 559) obtained ethyl thiacetoacetate on treating ethyl acetoacetate with thionyl chloride. In this reaction the thionyl chloride is decomposed into sulphur dichloride and sulphuryl chloride, which makes the formation of ethyl thiacetoacetate intelligible—

$$2SOCl_2 = SCl_2 + SO_2Cl_2.$$

Although the constitution of ethyl thiacetoacetate appeared sufficiently cleared up by the various syntheses and by Schönbrodt's saponification above mentioned, it seemed worth while to investigate it further, and to find other proofs of its constitution, since I had been unable to confirm Schönbrodt's analytical proof.

To this end, the best method of preparing ethyl thiacetoacetate was first studied, its physical properties were determined, and, finally, its behaviour towards the hydrazines was examined. In the reactions with hydrazines, a number of pyrazolone derivatives were obtained which are closely related to substances obtained by Knorr, the formation of which, as will be shown, affords new proofs of the constitution of ethyl thiacetoacetate.

Preparation of Ethyl Thiacetoacetate.

Ethyl acetoacetate is diluted with half its volume of chloroform, and the calculated quantity of sulphur dichloride dropped slowly into the mixture, which is well cooled and continuously stirred. The product is then allowed to remain until the evolution of hydrogen chloride has moderated; 82·3 grams of ethyl acetoacetate and 32·6 grams of sulphur dichloride yielded 58·8 grams of crude material, or 64 per cent. of the theoretical. For most purposes, ethyl thiacetoacetate can be obtained sufficiently pure if the crystals are collected and washed with a little cold ether. To obtain it pure, it must be crystallised from benzene, alcohol, or chloroform.

Different authors give very varying temperatures for the melting point of ethyl thiacetoacetate, so that it was necessary to redetermine the melting point carefully. According to Buchka, it melts at 81°. Deliole, however, was unable to assign a definite melting point for the substance crystallised out of alcohol, as he found that the crystals became soft at 75° and melted at 90—91°. Deliole gives the melting point 83—84° for crystals obtained from a solution in benzene. Schönbrodt assigns the melting point of 90° to ethyl thiacetoacetate; Michaelis and Philips, 100—101°. At first, I found very varying melting points for the crystals from a benzene solution, 92°, 99°, and 106°, and for the substance crystallised out of alcohol 82°. On repeating these experiments, heating the substance slowly in a water-bath which was continuously stirred, I found that ethyl thiacetoacetate three times crystallised out of alcohol melted at 75—76°, four times recrystallised at 79°; from a solution in benzene 75—78°, recrystallised from benzene 75—77°, crystallised out of glacial acetic acid 76°. If ethyl thiacetoacetate is heated slowly, it melts completely between 75° and 78°.

The Molecular Weight of Ethyl Thiacetoacetate.

The molecular weight of this substance was determined by Raoult's method. Glacial acetic acid was the solvent employed.

I. 1·4982 grams of ethyl thiacetoacetate was dissolved in 104·1 grams of glacial acetic acid of 16·105° melting point. The observed depression of the melting point was 0·215°, corresponding to a molecular weight of 261.

II. 2·0089 grams of substance dissolved in 109·5 grams of glacial acetic acid of 16·18° melting point caused a depression of 0·285°, corresponding to the molecular weight 251.

	Experiment.	
Theory.	I.	II.
290	261	251

Action of the Hydrazines on Ethyl Thiacetoacetate.

To determine whether ethyl thiacetoacetate behaved as a ketone, it was treated with phenylhydrazine, so as to be able to decide between the two constitutional formulæ previously mentioned (pp. 329, 330). The two react very readily, and when mixed in the proportion of 1 mol. ethyl thiacetoacetate to 2 mols. phenylhydrazine, give rise to the formation of four solid substances. The compounds produced are—

1. Thiophenylmethylpyrazolone.
2. Knorr's phenylmethylpyrazoloneazobenzene, or phenylmethylpyrazoloneketophenylhydrazone (*Annalen*, **238**, 183 and 197).
3. A substance of the empirical formula $C_{10}H_9N_2SO$.
4. Knorr's bisphenylmethylpyrazolone (*loc. cit.*, 167).

The end-product of the reaction is largely dependent on the conditions under which the experiment is carried out.

The first product of the reaction is the substance which I name *thiophenylmethylpyrazolone.*

Preparation.—5 grams of ethyl thiacetoacetate are dissolved in 90 grams of glacial acetic acid, well cooled, and then to this is added, drop by drop, a solution of 3 7 grams of phenylhydrazine in 30 grams of glacial acetic acid. The mixture, if allowed to remain at the ordinary temperature, turns reddish-brown, and, after some hours, yellowish crystals of the acetate are formed (*Ber.*, **23**, 2476); the yield is 8·8 grams. The substance can be purified by crystallisation from alcohol, to which some strong hydrochloric acid is added to convert it into the hydrochloride, which forms beautiful, colourless crystals.

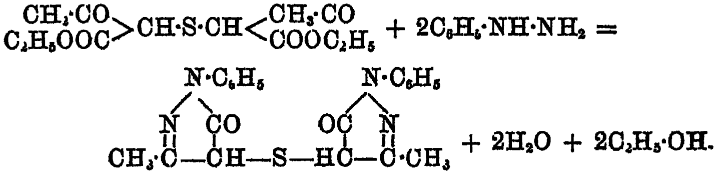
The substance for analysis was prepared by dissolving the hydrochloride in ammonia and precipitating the base with dilute acetic acid. In this way, it is obtained as a white, amorphous powder; it was collected on a filter, washed, dried first on a porous plate, then at 100°, and finally crystallised out of benzene or acetone. As in both cases the thiophenylmethylpyrazolone crystallises out with benzene or acetone of crystallisation, the crystals were heated at 110° in a stream of carbonic acid until the weight was constant, as they seem to suffer oxidation on heating in the air.

Analyses gave the following results:—

I. 0·2332 gram substance gave 0·5417 gram CO_2 and 0·1015 gram H_2O.
II. 0·2429 gram substance gave 0·5634 gram CO_2 and 0·1065 gram H_2O.
III. 0·2127 gram substance gave 27·1 c.c. moist nitrogen at 10° and 752 mm.
IV. 0·1995 gram substance gave 0·1243 gram $BaSO_4$.
V. 0·1996 gram substance gave 0·1225 gram $BaSO_4$.

	Experiment.		Theory for $C_{20}H_{18}N_4SO_2$.
	I.	II.	
C	63·33	63·27	63·44 per cent.
H	4·85	4·88	4·77 „
N	15·09	—	14·85 „
S	8·56	8·44	8·48 „

The formation of thiophenylmethylpyrazolone is as follows:—1 mol. of ethyl thiacetoacetate reacts with 2 mols. of phenylhydrazine with formation of water, alcohol, and a sulphur derivative of Knorr's phenylmethylpyrazolone.

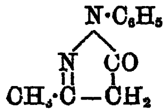


$$\begin{matrix}CH_3\cdot CO\\C_2H_5OOC\end{matrix}>CH\cdot S\cdot CH<\begin{matrix}CH_3\cdot CO\\COOC_2H_5\end{matrix} + 2C_6H_5\cdot NH\cdot NH_2 =$$

$$+ 2H_2O + 2C_2H_5\cdot OH.$$

This reaction is therefore completely analogous to the formation of phenylmethylpyrazolone from ethyl acetoacetate and phenylhydrazine (*Annalen*, **238**, 147; *Ber.*, **17**, 2033).

$$CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + C_6H_5\cdot NH\cdot NH_2 =$$



$$+ H_2O + C_2H_5\cdot OH.$$

Action of Sulphur Dichloride on Phenylmethylpyrazolone.

The above explanation of the reaction between phenylhydrazine and ethyl thiacetoacetate is confirmed by the circumstance that thiophenylmethylpyrazolone hydrochloride is formed when phenylmethylpyrazolone is treated with dichloride of sulphur. To prepare thiophenylmethylpyrazolone in this manner, 5 grams of phenylmethylpyrazolone are dissolved in just enough chloroform to prevent it crystallising out on cooling, and to this solution is added, drop by drop, 1·5 grams of sulphur dichloride, the mixture being kept cool until all the sulphur chloride has been added. On standing for a few hours, beautiful crystals of the hydrochloride crystallise out. To hasten the reaction, the mixture may be warmed gently on the water-bath, after it has stood for an hour. The crystals are collected and crystallised out of alcohol, in which they are moderately soluble; they contain alcohol of crystallisation, which seems to be firmly bound. The powdered crystals were left over sulphuric acid for a fortnight and then analysed.

0·2112 gram substance gave 0·1102 gram $BaSO_4$.

0·1877 gram substance gave 0·0590 gram AgCl.

	Experiment.	Theory for $C_{20}H_{18}N_4SO_2,HCl + C_2H_5\cdot OH$.
S	7·17	6·96
Cl	7·77	7·70

The hydrochloride was converted into the free base in the manner already described, by dissolving it in ammonia and precipitating with dilute acetic acid, collecting it, washing, drying, and crystallising out of benzene. The crystals were powdered and heated in carbonic acid until the weight was constant, and then analysed.

0·2326 gram substance gave 0·5419 gram CO_2 and 0·1017 gram H_2O.

0·2927 gram substance gave 36 c.c. moist nitrogen at 9° and 758 mm. pressure.

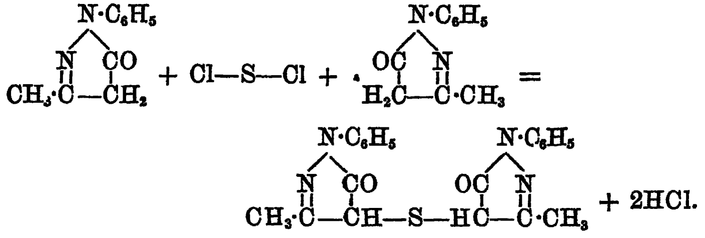
0·2476 gram substance gave 30·2 c.c. moist nitrogen at 7° and 763 mm. pressure.

0·1886 gram substance gave 0·1200 gram $BaSO_4$.

0·1909 gram substance gave 0·1190 gram $BaSO_4$.

	Experiment.		Theory for
	I.	II.	$C_{20}H_{18}N_4SO_2$.
C	63·54	—	63·44 per cent.
H	4·87	—	4·77 ,,
N	14·75	14·88	14·85 ,,
S	8·75	8·57	8·48 ,,

The analyses and the properties of this substance prove its identity with the compound obtained from ethyl thiacetoacetate and phenylhydrazine. Both substances decompose at the same temperature, 182—183°, show the same solubility, and give the same reactions. The formation of thiophenylmethylpyrazolone from sulphur dichloride and phenylmethylpyrazolone is given by the following equation:—



Properties of Thiophenylmethylpyrazolone.

Thiophenylmethylpyrazolone is characterised by its great power of crystallisation. It crystallises well from its solutions in alcohol, methyl alcohol, benzene, and acetone, and forms, in each case, a molecular compound with the solvent. The amorphous substance is more readily soluble than the crystals which are combined with a solvent. This is best seen when methyl alcohol is employed as the solvent; the amorphous substance dissolves readily, but in a very short time beautiful crystals form. Attempts to determine the amount of methyl alcohol, &c., in union with the substance gave only approximate results, as thiophenylmethylpyrazolone apparently loses the molecularly bound solvents easily, on exposure to the air.

0 3175 gram of crystals from an acetone solution lost 0·0393 gram at 110°, in an atmosphere of carbonic acid = 12·38 per cent.

The formula $C_{20}H_{18}N_4SO_2 + C_3H_6O$ requires 13·3 per cent. acetone of crystallisation.

0·2973 gram crystallised out of methyl alcohol lost 0·0201 gram in weight at 110°, in an atmosphere of carbonic acid = 6·76 per cent.

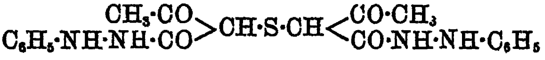
The formula $C_{20}H_{18}N_4SO_2 + CH_4O$ requires 7·81 per cent. methyl alcohol of crystallisation.

Thiophenylmethylpyrazolone is very little soluble in benzene. It is easily soluble in alkalis, forming colourless solutions, and is precipitated unchanged from these solutions by weak acids. In ammonia and baryta-water it dissolves with a yellow colour. Thiophenylmethylpyrazolone is a feeble base, and only forms salts with strong acids. It is easily soluble in concentrated sulphuric acid. On gently warming a mixture of thiophenylmethylpyrazolone (1 mol.) with

(1 mol.) phenylhydrazine in chloroform solution, it yields the three other above-mentioned products of the reaction between ethyl thiacetoacetate and phenylhydrazine, namely, phenylmethylpyrazoloneazobenzene, the substance $C_{10}H_9N_2SO$, and bisphenylmethylpyrazolone. The mixture was heated until all the chloroform had evaporated, and then left a short time longer on the water-bath. When heated with excess of phenylhydrazine without a diluent, thiophenylmethylpyrazolone only forms phenylmethylpyrazoloneazobenzene and bisphenylmethylpyrazolone. In the above-mentioned paper by Michaelis and Philips, these authors describe a colourless substance which they obtained by the condensation of ethyl thiacetoacetate with phenylhydrazine in a solution of glacial acetic acid. Analyses of this substance, purified by crystallisation from alcohol, led them to the formula $C_{20}H_{22}O_4N_4S$.

	Experiment.	Theory.
N	13·30	13·50 per cent.
S	7·74	7·73 „
C	58·15	57·97 „
H	5·55	5·31 „

Michaelis and Philips suggest, with reserve, the constitution



$$\begin{matrix}CH_3\cdot CO \\ C_6H_5\cdot NH\cdot NH\cdot CO\end{matrix}>CH\cdot S\cdot CH<\begin{matrix}CO\cdot CH_3 \\ CO\cdot NH\cdot NH\cdot C_6H_5\end{matrix}$$

for this substance, according to which view it is a hydrazide of the unknown thiacetoacetic acid. It decomposes at 185°, is sparingly soluble in alcohol and glacial acetic acid, and on heating with phenylhydrazine gives Knorr's phenylmethylpyrazoloneazobenzene and hydrogen sulphide. From the method of formation of this substance, and its properties, it is obvious that it is thiophenylmethylpyrazolone, the circumstance that Michaelis and Philips found different analytical data being due to the fact that they overlooked the alcohol of crystallisation.

The Second Product of the Reaction, Knorr's Phenylmethylpyrazoloneazobenzene (*Annalen*, 238, 183 and 197).

To prepare this substance, a mixture of 1 mol. of ethyl thiacetoacetate with 4 mols. of phenylhydrazine is heated without a diluent at a temperature of 100° until the evolution of hydrogen sulphide ceases. It is a good plan to carry out this reaction in an atmosphere of carbonic acid, so as to prevent oxidation of the phenylhydrazine. Under the above conditions, a red hydrazone is almost the sole product of the reaction, a little bisphenylmethylpyrazolone being formed at the same time. The red substance, after purification by crystallisation from alcohol, melted at 156°. It is soluble in chloroform, benzene, alcohol, ether, and glacial acetic acid.

Analyses gave the following data:—

I. 0·2670 gram substance gave 0·6808 gram CO_2 and 0·1466 gram H_2O.

II. 0·2410 gram substance gave 0·6128 gram CO_2 and 0·1175 gram H_2O.

III. 0·1718 gram substance gave 30·2 c.c. moist nitrogen at 8° and 742 mm. pressure.

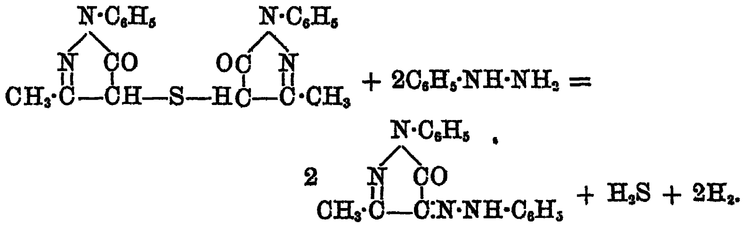
IV. 0·2491 gram substance gave 44·7 c.c. moist nitrogen at 21° and 745 mm. pressure.

V. 0·1361 gram substance gave 25·1 c.c. moist nitrogen at 19° and 751 mm. pressure.

	Experiment.					Theory for $C_{16}H_{14}N_4O$.
	I.	II.	III.	IV.	V.	
C......	69·54	69·34	—	—	—	69·01 p. c.
H......	6·10	5·41	—	—	—	5·04 „
N......	—	—	20·72	20·01	20·94	20·14 „

It is identical, therefore, with Knorr's phenylmethylpyrazoloneazobenzene.

The formation of this substance from ethyl thiacetoacetate may be explained as follows. In the first place, 1 mol. of ethyl thiacetoacetate reacts with 2 mols. of phenylhydrazine, forming thiophenylmethylpyrazolone, which with 2 mols. more phenylhydrazine gives rise to the following reaction:—



The hydrogen sulphide was recognised by means of lead acetate paper. The nascent hydrogen reduces a part of the phenylhydrazine to aniline and ammonia.

The Third Product of the Reaction, $C_{10}H_9N_2SO$.

To prepare this, ethyl thiacetoacetate is mixed with phenylhydrazine in the ratio of 1 to 2 mols., and the mixture heated at 100 until the whole mass solidifies. The yield depends on the conditions under which the reaction is carried out; a high temperature is to be avoided. The substance is practically insoluble in all the usual solvents, but is easily soluble in alkalis, ammonia, and the hydrates of the alkaline earths. It was purified for analysis by repeated extraction with alcohol, then dissolved in ammonia, the ammoniacal solution filtered, and the substance precipitated by means of dilute acetic acid. The yellowish, amorphous substance was filtered, washed, and dried at 100°.

Analyses gave the following results:—

I. 0·1833 gram substance gave 0·3950 gram CO_2 and 0·773 gram H_2O.
II. 0·1765 gram substance gave 0·3777 gram CO_2 and 0·0731 gram H_2O.
III. 0 1766 gram substance gave 21·7 c.c. moist nitrogen at 22° and 752 mm. pressure.
IV. 0·1628 gram substance gave 19·7 c.c. moist nitrogen at 25° and 756 mm. pressure.
V. 0·2183 gram substance gave 0·2612 gram $BaSO_4$.
VI. 0·2011 gram substance gave 0·2432 gram $BaSO_4$.

	I.	II.	III.	IV.	V.	VI.	
C	58·75	58·34	—	—	—	—	p. c.
H	4·69	4·61	—	—	—	—	,,
N	—	—	13·77	13·43	—	—	,,
S	—	—	—	—	16·44	16·62	,,

I attributed to this substance the formula $C_{10}H_8N_2SO$, which requires

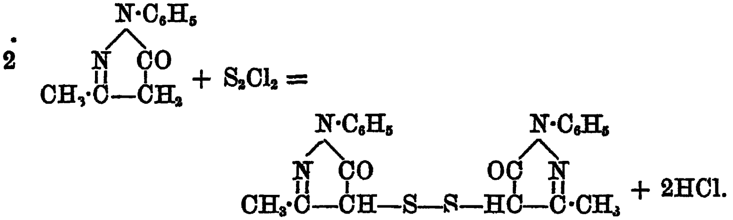
C	58·77 per cent.
H	3·93 ,,
N	13·76 ,,
S	15·70 ,,

but, since my research, Höltzcke, who has further investigated this substance, has shown that it is the bisulphide of phenylmethylpyrazolone, which requires

C	58 49 per cent.
H	4·40 ,,
N	13·69 ,,
S	15·63 ,,

Höltzcke obtained it by the action of chloride of sulphur on a solution of phenylmethylpyrazolone in chloroform.

The reaction is as follows:—



When treated with phenylhydrazine, the bisulphide is converted into Knorr's phenylmethylpyrazoloneazobenzene and bisphenylmethylpyrazolone, hydrogen sulphide being also formed. By means of the above reaction it is possible to obtain mixed hydrazones of the pyrazole series by acting on the bisulphide with other hydrazines. α-Naphthylhydrazine, for instance, forms a brown-red compound which melts at 199 5°.

The bisulphide is soluble in boiling aniline, and is thereby converted into a colourless substance sparingly soluble in alcohol; it decomposes without melting, and gives the pyrazole-blue reaction. The substance is accordingly bisphenylmethylpyrazolone.

The Fourth Product of the Reaction, Knorr's Bisphenylmethylpyrazolone (Annalen, 238, 167).

This substance and phenylmethylpyrazoloneazobenzene are the final solid products of the reaction between ethyl thiacetoacetate and phenylhydrazine It was identified by means of Knorr's pyrazole-blue reaction, for on dissolving it in alkali and adding potassium nitrite, the mixture gave a dark-blue substance when poured into dilute sulphuric acid; this was soluble in chloroform, yielding a deep blue solution.

The behaviour of ethyl thiacetoacetate towards other hydrazines is completely analogous to that with phenylhydrazine.

Condensation Products of Ethyl Thiacetoacetate with Paratolylhydrazine.

Four products were also formed in this reaction, viz.:—

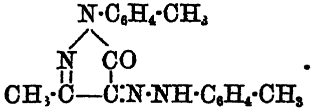
1. A colourless substance soluble in alcohol.
2. A red hydrazone, paratolylmethylpyrazoloneketoparatolylhydrazone.
3. A substance containing sulphur, insoluble in alcohol.
4. A substance free from sulphur, insoluble in alcohol, bisparatolylmethylpyrazolone.

The first-mentioned substance was not analysed, but from analogy it is to be regarded as thioparatolylmethylpyrazolone.

Paratolylmethylpyrazoloneketoparatolylhydrazone.

To obtain the best yield of this substance, 1 mol. of ethyl thiacetoacetate is mixed with 4 mols. of paratolylhydrazine and the mixture heated at 120° to 150° in a stream of carbonic acid until the evolution of gas ceases. 1·7 grams of ethyl thiacetoacetate and 2·8 grams of paratolylhydrazine yielded 0·4 gram of substance; this was extracted from the product of the reaction by means of chloroform, the solution filtered, evaporated to a small bulk, and the hydrazone precipitated by the addition of 90 per cent. alcohol.

By dissolving the substance in a little chloroform and precipitating it with alcohol, it may be easily obtained pure. It melts at 216—217°. The analyses prove that the substance is paratolylmethylpyrazoloneketoparatolylhydrazone,



$$\begin{array}{c} N{\cdot}C_6H_4{\cdot}CH_3 \\ N \quad CO \\ CH_3{\cdot}C—C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3 \end{array}.$$

I. 0·1755 gram substance gave 0·4537 gram CO_2 and 0·0945 gram H_2O.

II. 0·1258 gram substance gave 21·1 c.c. moist nitrogen at 21° and 750 mm. pressure.

III. 0·1992 gram substance gave 33·5 c.c. moist nitrogen at 24° and 749 mm. pressure.

	Experiment.			Theory for
	I.	II.	III.	$C_{18}H_{18}N_4O$.
C........	70·48	—	—	70·53 p. c.
H........	5·99	—	—	5·89 „
N........	—	18·84	18 58	18·34 „

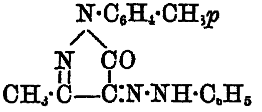
This substance, unlike the corresponding phenyl compound, is but sparingly soluble in alcohol, ether, and alkalis. It is easily soluble in chloroform, from which it crystallises in beautiful needles.

The Third Product of the Reaction, the Substance containing Sulphur and insoluble in Alcohol.

6·4 grams of ethyl thiacetacetate (1 mol.) were heated with 5·2 grams of paratolylhydrazine at 120° for two hours, and gave 4·8 grams of the substance. I attempted to purify it by extraction with chloroform and alcohol as well as by dissolving it in alkali and precipitating with dilute acetic acid, but the analysis did not give satisfactory results.

The product is soluble in alkali and ammonia with formation of yellow solutions, from which it is precipitated unchanged by the addition of an acid. A solution of the substance in alkali gives no pyrazole-blue reaction with nitrous acid, but is precipitated apparently unchanged.

The following reaction shows that it is analogous to dithiophenylmethylpyrazolone; when heated with phenylhydrazine, it evolves hydrogen sulphide, and a red hydrazone, namely, paratolylmethylpyrazoloneketophenylhydrazone, is produced,



.

To obtain the latter, the insoluble sulphur compound was heated with excess of phenylhydrazine at 120—150° until there was no longer any evolution of gas; the excess of phenylhydrazine was then removed by boiling the product with dilute hydrochloric acid and washing with hot water; the red residue was dissolved in a little chloroform, the solution filtered off from the insoluble bisparatolylmethylpyrazolone which is also formed in the reaction, and the filtrate mixed with excess of 90 per cent. alcohol and well stirred. In this way, nearly the whole of the hydrazone is precipitated in the crystalline state, and can be easily obtained pure by redissolving in chloroform and precipitating with alcohol. The crystals are of a beautiful scarlet colour and melt at 187°.

0·1275 gram substance gave 20·5 c.c. moist nitrogen at 11° and 759 mm. pressure.

	Experiment.	Theory for $C_{17}H_{16}N_4O$.
N	19·15	19·22 per cent.

It is sparingly soluble in alcohol, but easily in chloroform.

Bisparatolylmethylpyrazolone.

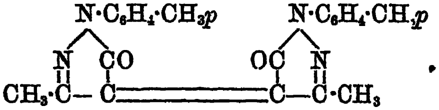
2·5 grams of ethyl thiacetoacetate and 4·2 grams of paratolylhydrazine were heated at 120—230° in a stream of carbonic acid for about two hours. On extracting the product of the reaction with chloroform, 2·2 grams of a yellowish-white substance remained undissolved; this was purified by boiling, at first with chloroform and alcohol, then with carbon bisulphide, collecting the residue, washing well with absolute alcohol, and dissolving it in dilute caustic potash. The solution was now filtered, the substance precipitated with dilute hydrochloric acid, and the precipitate, after being collected, washed with water, and dried at 100°, was submitted to analysis, with the following results:—

I. 0·1990 gram substance gave 0·5169 gram CO_2 and 0·1110 gram H_2O.

II. 0·2019 gram substance gave 28 c.c. moist nitrogen at 21° and 741 mm. pressure.

	Experiment.		Theory for $C_{22}H_{22}N_4O_2$.
	I.	II.	
C	70·85	—	70·53 per cent.
H	6 21	—	5·89 ,,
N	—	15·38	15·01 ,,

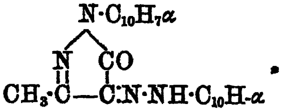
If this substance is dissolved in alkali, and potassium nitrite added to the solution and the mixture poured into dilute sulphuric acid, a blue substance is precipitated which is soluble in chloroform, and which is probably a dimethylpyrazole blue,



Its formation is completely analogous to that of pyrazole blue from bisphenylmethylpyrazolone. Bisparatolylmethylpyrazolone is insoluble in all neutral solvents, but is readily soluble in alkalis, less so in ammonia. Like bisphenylmethylpyrazolone, it is not changed by heating with phenylhydrazine. From the above, it is clear that ethyl thiacetoacetate reacts with paratolylhydrazine in a manner entirely analogous to its behaviour with phenylhydrazine. The only difference in the reaction is that the hydrazone in this case is formed in relatively smaller quantity, and bisparatolylmethylpyrazolone in relatively larger quantity, than the corresponding phenylhydrazine derivatives.

α-Naphthylmethylpyrazoloneketo-α-naphthylhydrazone.

Of the condensation products of α-naphthylhydrazine and ethyl thiacetoacetate, only the above substance was prepared and examined. It has the constitution



Preparation.—2 9 grams of ethyl thiacetoacetate (1 mol.) and

6·3 grams of α-naphthylhydrazine were heated for three hours at 120° in an atmosphere of carbonic acid. A considerable quantity of a red substance was formed, which was purified by dissolving in chloroform, filtering, and precipitating with alcohol. The pure substance melted at 220°, and gave the following data on analysis:—

I. 0·1955 gram substance gave 0·5458 gram CO_2 and 0·0886 gram H_2O.

II. 0·1959 gram substance gave 24·5 c.c. moist nitrogen at 11° and 762 mm. pressure.

	Experiment.		Theory for $C_{24}H_{18}N_4O$.
	I.	II.	
C	76·14	—	76·15 per cent.
H	5·04	—	4·77 ,,
N	—	14·95	14·84 ,,

This substance is very little soluble in alcohol, but, like the analogous compounds, easily in chloroform.

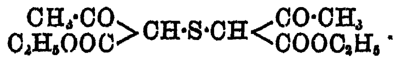
Summary of Results.

The reaction of the hydrazines on ethyl thiacetoacetate takes place in three stages:—

1. In the first instance, a pyrazolone sulphide is formed from 2 mols. of a hydrazine and 1 mol. of ethyl thiacetoacetate.

2. These sulphides are, however, decomposed by excess of phenylhydrazine into insoluble pyrazolone bisulphides, and into bisphenylmethylpyrazolone or one of its homologues.

3. The pyrazolone bisulphides finally react with hydrazines with formation of hydrogen sulphide and hydrazones of the pyrazole series, and by means of this reaction mixed hydrazones can be obtained. From the above, it is clear that ethyl thiacetoacetate behaves towards phenylhydrazine in the same manner as ethyl acetoacetate, which fact affords further proof that the constitution of ethyl thiacetoacetate is



$$\begin{matrix}CH_3\cdot CO\\C_2H_5OOC\end{matrix}>CH\cdot S\cdot CH<\begin{matrix}CO\cdot CH_3\\COOC_2H_5\end{matrix}.$$

In the case of ethyl thiacetoacetate the reaction is more complicated, since the entrance of the sulphur atom into the methylene group diminishes its stability, and also since excess of a hydrazine easily removes the sulphur atom as hydrogen sulphide, thus giving rise to the formation of complicated pyrazolone derivatives.

In conclusion, I have to express my best thanks to Professor von Buchka for the valuable assistance he rendered me during this investigation.

XLI.—*On the Osmotic Pressures of Salts in Solution.*

By R. H. Adie, M.A., Trinity College, Cambridge.

In a paper in the *Zeit. physikal. Chem.*, **1**, 481, Van't Hoff discusses the analogy between the osmotic pressure of a salt in solution and the pressure exerted by a gas on the walls of its containing vessel.

The numbers upon which he bases the verification of his calculations were obtained by Pfeffer, in his *Osmotische Untersuchungen* (Leipzig, 1877), and only embrace the figures for a few salts, viz., potassium nitrate, potassium tartrate, and for the complex organic substances cane sugar, and gum arabic. These were the only independent measurements of osmotic pressures in absolute units, until A. Ladenburg published (*Ber.*, **22**, 1225) a few numbers for the osmotic pressures of solutions of dextrose, resorcinol, cane sugar, and "saccharin."

It is not easy to get actual measurements of osmotic pressures, but a number of comparisons of the osmotic pressures of different salts in solution were made by De Vries (*Pringsheim's Jahrb.*, **14**; *Zeit. physikal. Chem.*, **2**, 415; **3**, 103), who found the concentrations of isotonic solutions of these salts, by means of the exosmotic contractions which they bring about in the protoplasmic lining membrane of living cells.

In very dilute solutions, the substances examined appeared to obey the laws of Boyle, Gay-Lussac, and Avogadro, but in the case of strong solutions, the deviations were considerable.

At the suggestion of Professor J. J. Thomson, I took in hand the direct measurement of osmotic pressures by Pfeffer's method, but the length of time required by each experiment renders the accumulation of results very slow.

The method consists in depositing a membrane in the substance of a porous pot, which membrane must be continuous, and coarse-grained enough to allow the passage of water molecules through its interstices, but sufficiently fine-grained to prevent the passage of salt molecules, or the compound molecules of a salt, and water; a salt solution placed within such a pot gets up a pressure when placed in pure water. I have tried in various ways to form a membrane capable of withstanding a pressure of 3—4 atmos. without giving way, and have finally returned to the simple form of apparatus which is drawn in section in Fig. 1.

It consists of a porous pot, B, in which the membrane is deposited, connected with a simple manometer gauge, AC, which is connected with B by means of the glass adapter E.

I describe the parts in detail, as they are the product of considerable experimental work.

FIG. 1*a*.

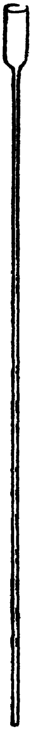
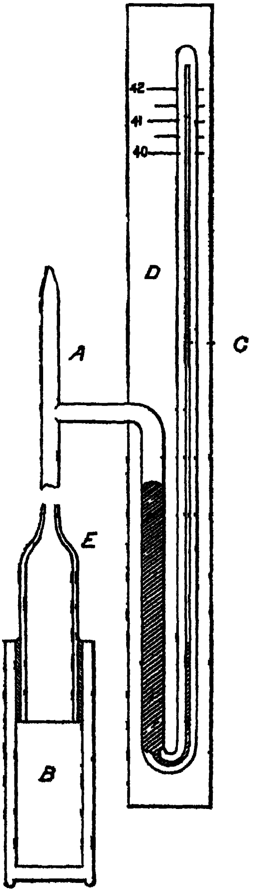


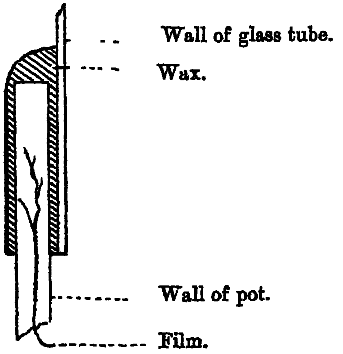
FIG. 1.



The Pots.

The only porous pots found to give any consistent results are specially made of biscuit porcelain, 3 inches long, 1 inch external diameter, and $\frac{3}{16}$-inch substance. Into the open end, a tightly fitting glass tube E (Fig. 1), drawn off at one end, is inserted and fixed for a length of about 1 inch, by sealing wax. No wax is put on the outside, for experience shows that, in this case, the membrane is formed irregularly between the two layers of wax. This is shown by Fig. 2, which is a section of the wall of such a pot. As the membrane generally gives way at the top (perhaps the pores of the pot are coarser there, due to the method of manufacture), it is essential to give it a good connection with a solid wall of wax some way down the pot.

FIG. 2.



Some other methods were tried for getting the top secure: (i) supporting the upper end of the membrane by melting paraffin wax into the top of the pot, after a preliminary formation of the membrane and drying the pot; this did not give good results; (ii) having the upper ends of the pot glazed with porcelain glaze, but as the glaze could only be applied superficially inside and out, instead of throughout the mass of the biscuit, the membrane-forming solutions did not diffuse evenly, and the film was formed irregularly, and even locally, between the two layers of glaze, and when a high internal pressure was maintained for some time, it forced the solutions through minute cracks in the glaze. This is shown in section in Fig. 3. Messrs. Morlent Frères, Bayeux, kindly tried to glaze some throughout, but did not succeed.

The 1-inch long sealing wax joint withstands pressures of 3½ to 4½ atmos., depending on the temperature, and at the same time prevents the membrane from approaching the top of the pot, since the outer solution has diffused over ½ inch downwards from the top, before it reaches the inner solution. This is shown in section in Fig. 4.

The dimensions of the pots allow all the connections and fittings to be made of glass.

Up to the present, sealing wax is the only cement with which I have been able to get any results, with one exception.

FIG. 3.

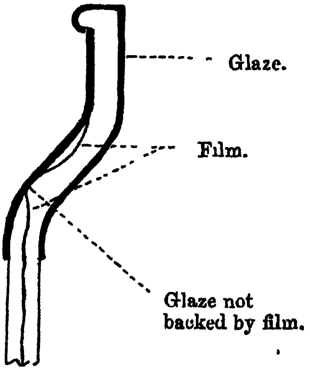
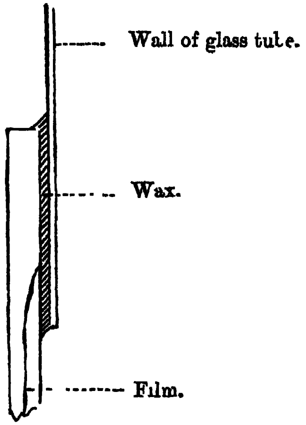


FIG. 4.



For temperature experiments it is necessary to use another cement. Portland cement is too porous to form a strong film, and the free alkali in it decomposes the copper sulphate solution used. The pressures obtained with this cement are only about one-half those got with sealing wax.

The double phosphate of zinc and sodium, and the oxychloride of zinc both make good cements, but only become hard when the zinc oxide used is prepared by heating the nitrate. This oxide is very hard, and requires careful and prolonged grinding before it is sufficiently fine to use. When made, the cement sets very quickly, and is difficult to manipulate. However, the only temperature experiment I have been able to complete was made with a pot fixed with the sodiophosphate cement.

The Membrane.

Pfeffer in his researches used a membrane of copper ferrocyanide formed by precipitation from 3 per cent. solutions of copper sulphate, and potassium ferrocyanide, when these were allowed to diffuse from each side of a porous pot which had been immersed in the copper sulphate solution, and partially dried. He also experimented with membranes of calcium phosphate, ferric hydroxide, ferrous carbonate, and ferric ferrocyanide, and found that they did not prevent the passage of salts so completely as the copper compound. I also tried the same membrane and, in addition, aluminium hydroxide, and silicic, and tungstic acids, but could not get satisfactory results with the commercial pots, except with ferric ferrocyanide. The specially manufactured pots gave excellent results with the copper salt, and so saved further experiment.

The chief objection to the ferrocyanide film is that the solutions which surround it must be neutral, or at any rate not dissociated* in solution. On the other hand, the destruction of the film is an excellent, but trying proof that a salt is dissociated in solution.

The Gauge.

A simple form of manometer was found to give good results, since it could be attached to the pot by the help of a blowpipe, after the film was made (Fig. 1, p. 345). C is a capillary tube of uniform bore about 45 cm. long. The rest of the tubing is about $\frac{3}{16}$ inch bore. The heights were read sufficiently accurately by the millimetre scale D.

Mode of Preparing the Membranes and Setting up the Apparatus.

At first I tried Pfeffer's method of depositing the membranes, but could not get a strong film by it. The following, based on a suggestion of Professor J. J. Thomson's assistant, Mr. E. Everett, was, however, found to give excellent results :—

The clean and dry pot with its glass tube attached is gradually lowered into the copper sulphate solution, while the ferrocyanide solution is being poured into the inside. The pots are then placed under the air pump and kept in a vacuum for some days till all the air is drawn out of their pores. They are then allowed to stand about three weeks in more dilute solutions, to thicken up any weak places in the film. Too long standing in a vacuum is apt to cause a precipitation of copper oxide on the outside of the pot, and this seems to interfere with the free passage of water.

The film thus formed at the first contact of the two liquids is right in the middle of the pot walls, and stands pressures up to 4½ atmos.

When ready for use, the pots are attached to their gauges by the blowpipe.

It is easy to empty the pots through the drawn-out tube A, by means of a piece of tube drawn out into a long capillary (Fig. 1*a*), and a suction pump. They are filled by a wash-bottle, or pipette with a capillary delivery tube.

In order to select the pots which can be used, they are filled with a salt solution which will get up a pressure of about 1 atmo. A solution of potassium nitrate $\frac{1}{20}$ gram mol. per litre does for this purpose, but solutions of $\frac{1}{40}$ gram mol. of potassium sulphate per litre or of $\frac{1}{80}$ gram mol. of potash alum per litre are better, as they keep their maximum pressures constant for a longer time than the nitrate. If a stronger solution is used at first, the film very often bursts.

---

* Throughout this paper the term "dissociation" is used in its ordinary acceptation of dissociation into constituents. When dissociation into ions is meant, the words "into ions" have been inserted in the text.

Only about 25—30 per cent. of the pots set up give satisfactory results.

Pots which gave results nearly a maximum on their trials were used for testing Boyle's law in solutions. but only those which gave the maximum were used for observations which had to be compared with those from other pots.

When not in use, the pots were filled with, and stood in, distilled water. That this does not affect the film was shown by the fact that a pot (ϵ and ξ_3) which was kept standing in water for about a year gave practically the same results after this interval as it did before.

The Observations.

Owing to the thickness of the pot and the distance of the membrane from the inner surface, washing, &c., which requires the help of diffusion, takes a long time.

As the solutions used are very dilute (about 0·5—3 per cent.), it is necessary to remove any excess of salt left in the pot walls by the last solution. The pot is first thoroughly washed with distilled water, in order to remove any salt solution adhering to the sides of the pot and tubes, but to extract the salt contained in the pores it is necessary to fill the pot with distilled water and allow it to stand in distilled water for 24 hours.

The small percentage of salt in the pores causes a current of water through the film from the outside, which assists the washing as well as the diffusion. This treatment is generally sufficient to remove traces of the last occupant, though it is advisable to wash for 2—3 days, when time allows, and the consecutive solutions are not isotonic. (For examples see I.)

The pot is now filled with the new solution, allowed to stand for 24 hours, and then refilled. When the temperature is constant, readings are taken of the top of the air column of gauge, *a*; the level of mercury, *b* and *c*, in both limbs of the U-tube; the upper level of the solution, *d*, in A (p. 345); the barometric height, *e*; and the temperature, *f*. These give us the initial values for the volume and pressure of the air in the manometer gauge, v_0 and p_0.

The top of A is now sealed, and these readings taken daily till the pressure is constant. For a good pot it does not seem necessary, though advisable in some cases, to take readings oftener than once a day, as the final pressure keeps constant for 1—3 days, according to the solution.

When constant, the diminished volume of the air, v, in the gauge is read, and the pressure calculated by Boyle's law.

p_0 is obtained by correcting the atmospheric pressure for the difference of level of the mercury in the two limbs of the U-tube, and also for the column of solution in A. p_1 is corrected for the difference of the mercury levels, for the atmospheric pressure on the water surrounding the pot, and for the difference of level between this water and the mercury column in communication with the pot. The last correction may be obviated by making the water-level of the vessel in which the pot is immersed the same as that of the mercury column.

A correction for dilution of the original solution by the entry of water to take the place of the mercury in the gauge has been avoided by making the capacity of the apparatus considerable, with respect to the bore of the gauge-tube C, and by making the amount of air enclosed in A very small also.

The time taken by the salt to get up its maximum pressure depends partly on the pot and partly on the character of each salt. A slow rate of rise is usually the characteristic of a strong and lasting film, but I have had a few exceptions.

Neutral salts do not in general attack the membrane, but some curious exceptions were noted. Ordinary potash alum and ammonia alum are not dissociated in solution; chrome alum gradually attacks the film. Potassium nitrate and many others (see below, V) are not dissociated; sodium nitrate gradually attacks the film. Potassium, calcium, ammonium, and aluminium sulphates are not dissociated; sodium, magnesium, and copper sulphates are dissociated. Potassium ferricyanide is dissociated, whilst the cobalticyanide is not. Potassium hydrogen carbonate gradually weakens the film, and trisodium phosphate, as might be expected, destroys it at once. In fact, it appears that the potassium salts of the strong acids are the least dissociated, whilst the sodium salts of these acids are much more generally dissociated.

This might almost be expected from the position of sodium in the periodic arrangement of the elements, in the same section of the first group as hydrogen, and from the behaviour of acids towards the film, but at the same time it is possible that the action is not due to simple dissociation, but to a specific action of the sodium salts, caused by their being relatively less completely saturated than the corresponding potassium salts. If this be the case, there ought to be some difference between the two in their action as solvents of more complex compounds. The only case which suggests itself is the incomplete precipitation of the paraglobulins from solution by means of sodium salts as compared with other neutral salts, though I am not aware of any comparative trials of the potassium salts.

The destruction and breaking down of the film may be either sudden, or gradual. The gradual breaking down is shown in the lower curves of K_2SO_4 in ρ_2, in Fig. 7 (p. 354), and of potash alum in γ, in Fig. 15 (p. 361), where the curve takes the same form as in the case of known dissociation of chrome alum in Fig. 16 (p. 362).

The phenomena of dissociation of simple, and of double salts in solution has been investigated by F. Rüdorff (*Ber.*, **21**, 4, 3044). He shows that many of these are dissociated, and may be separated into their constituents by diffusion through a porous cell into water.

In the following tables, the temperature at which the osmotic pressures were taken varies from 15° to 19°: this does not introduce any appreciable error in the pressures estimated in atmospheres, and in the Boyle's law observations the variation of temperature of the consecutive observations is less than 2°.

The quotient P/π, which is the same numerically as Arrhenius' coefficient of dissociation, i, is the number of times the observed pressure, P, is greater than that π, calculated on the assumption that the ultimate osmotic pressure is the same as would be exerted by the compression of a gram-molecule of hydrogen into the same space as the solution occupies. The values of π are for

$$\frac{1}{160} \text{ gram-mol. per litre} = 0{\cdot}14 \text{ atmo.}$$

and for $$n \times \frac{1}{160} \quad \text{,,} \quad \text{,,} \quad = n \times 0{\cdot}14 \text{ atmo.}$$

This should be corrected for temperature, and at 15° becomes $n \times 0{\cdot}1475$.

It may also be convenient to remember that at 15° a pressure of 1 atmo. would be produced by 0·424 gram-molecule per litre.

I. *Boyle's Law applied to Salts in Solution.*

In the following tables column I is the strength of the solution in gram formula weights per litre; column II the osmotic pressure in atmospheres; column III the quotient P/π, or i, the dissociation coefficient.

The results will be found plotted out in Figs. 5 and 10.

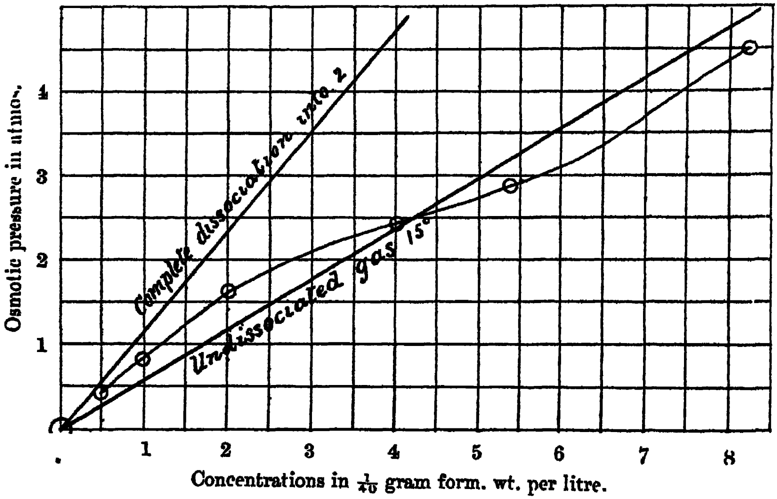
1. *Simple Salts.*

a. Solution of KNO_3 in different pots. Fig. 5.

I.	II.	III.
$\frac{1}{5}$ (nearly)	4·50	1·04
$\frac{1}{7·5}$	2·87	0·96
$\frac{1}{10}$	2·39[1]	1·07
$\frac{1}{20}$	1·56[2]	1·39
$\frac{1}{40}$	0·89[3]	1·59
$\frac{1}{80}$	0·466	1·66

[1] Mean of 2·39, 2·41, 2·37.
[2] Mean of 1·76, 1·48, 1·38, 1·61, 1·49, 1·64.*
[3] Mean of 0·96, 0·82.

KNO_3. FIG 5.



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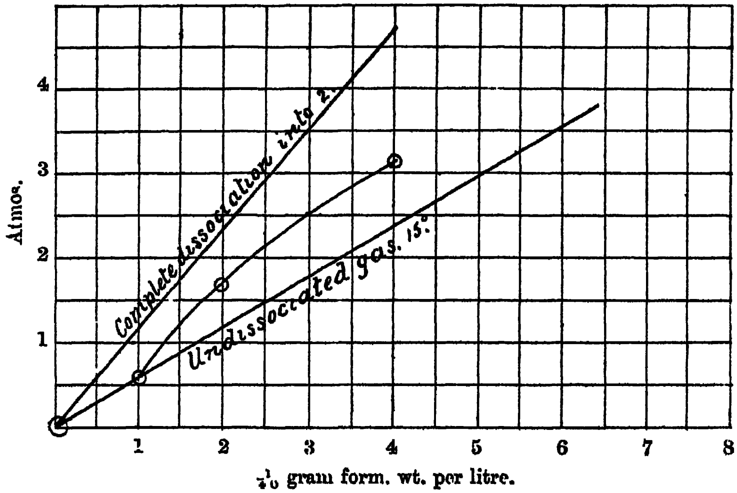
* These figures were obtained for the nitrate when used as the first solution, for trying the pots. Hence they differ more than the others.

b Solution of $NaNO_3$ in different pots. Fig. 6.

I.	II.	III.
$\frac{1}{10}$	3·11	1·39
$\frac{1}{20}$	1·69[4]	1·51
$\frac{1}{40}$	0·60	1·67

[4] Mean of 1·79, 1·59.

$NaNO_3$. FIG. 6.

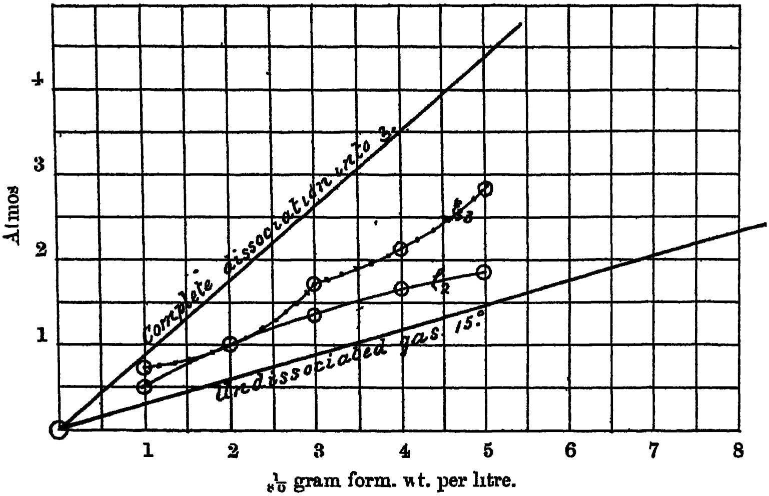


c. Solution of K_2SO_4. Fig. 7 (p. 354).
Series (i) in one pot p_3. In order starting with strongest.

I.	II.	III.
$\frac{5}{80}$	1·895	1·35
$\frac{4}{80}$	1·68	1·50
$\frac{3}{80}$	1·38	1·65
$\frac{2}{80}$	1·02[1]	1·82
$\frac{1}{80}$	0·505	1·81

[1] Mean of 1·05, 0·99.

K_2SO. FIG. 7.



Series (ii) in one pot ξ_3, in following order: 2, 4, 1, 3, 5 × $\frac{1}{80}$.

I.	II.	III.
$\frac{5}{80}$	2·82	2·01
$\frac{4}{80}$	2·19	1·96
$\frac{3}{80}$	1·705	2·03
$\frac{2}{80}$	1·01	1·81
$\frac{1}{80}$	0·66	2·36

d. Solution of $(NH_4)_2SO_4$ in one pot τ.

I.	II.	III.
$\frac{1}{20}$	2·64	2·36
$\frac{1}{40}$	1·30	2·33

e. Solution of $CaSO_4$ in one pot o_2..

I.	II.	III.
$\frac{1·148^2}{80}$	0·467	1·59
$\frac{0·574}{80}$	0·245	1·67

---

[2] This is a saturated solution.

f. Solution of KI in one pot o_2. Fig. 8.

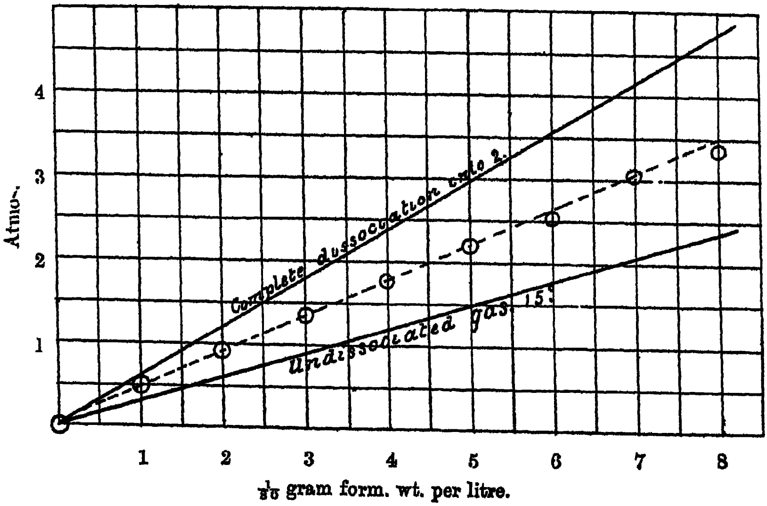
I.	II.	III.
$\frac{8}{80}$	3·37[1]	1·50
$\frac{7}{80}$	3·05	1·56
$\frac{6}{80}$	2·56[2]	1·52
$\frac{5}{80}$	2·21	1·57
$\frac{4}{80}$	1·775[3]	1·58
$\frac{3}{80}$	1·35	1·61
$\frac{2}{80}$	0·92	1·64
$\frac{1}{80}$	0·496	1·77

[1] $\xi_3 = 3{\cdot}31.$

[2] $\zeta_3 = 2{\cdot}22.$

[3] $\delta = 1{\cdot}81.$

KI. Fig. 8.



2. *Hydrogen Salts.*

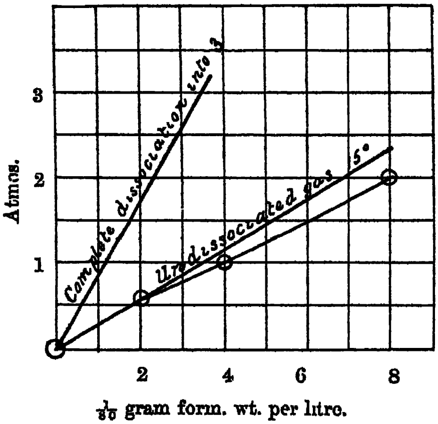
a. Solution of $KHCO_3$ in one pot ρ_2. Fig. 9.

I.	II.	III.
$\frac{8}{80}$	2·03	0·91
$\frac{4}{80}$	1·01[1]	0·90
$\frac{2}{80}$	0·59[2]	1·05

[1] Mean of 0·95, 1·07.
Duplicate from $\delta = 1·32$.
[2] Duplicate from $\delta = 0·655$.

FIG. 9.

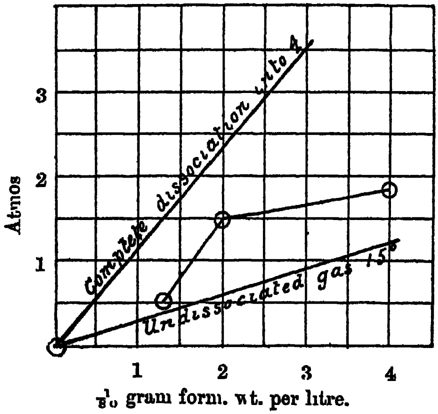
KHCO₃.



b. Solution of Na_2HPO_4 in one pot ν. Fig. 10 (p. 357).

I.	II.	III.
$\frac{4}{80}$	1·82	1·62
$\frac{2}{80}$	1·50	2·68
$\frac{1}{80}$	0·51	1·40

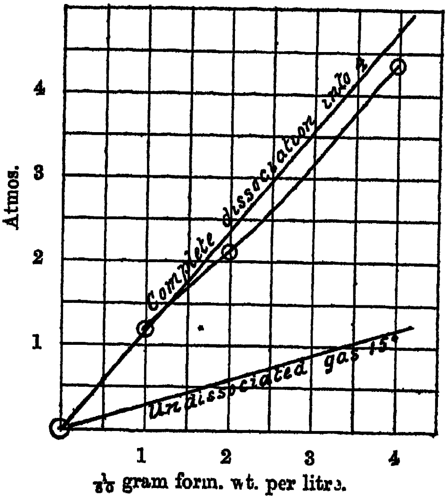
Na_2HPO_4. FIG 10.



c. Solution of Na_2HCi in one pot π_2. Fig. 11.

I.	II.	III.
$\frac{1}{20}$	4·32	3·86
$\frac{1}{40}$	2·12	3·79
$\frac{1}{80}$	1·23	4·40

Na_2HCi. FIG. 11.

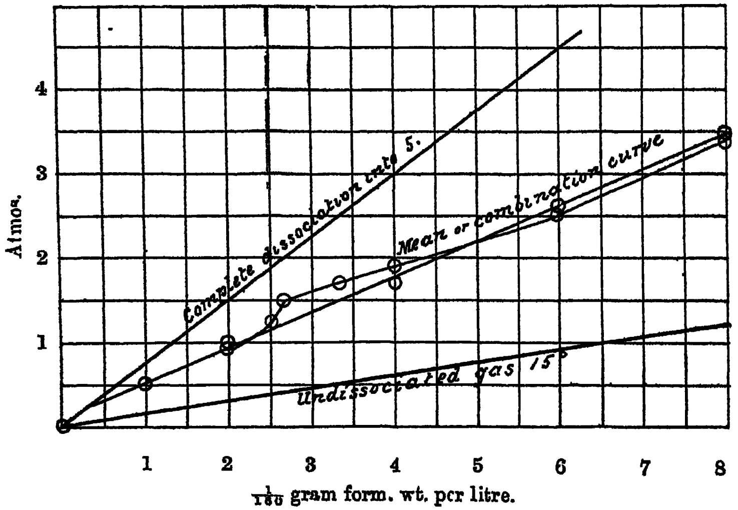


3. *Salts of Compound Acids.*

a Solutions of $K_4FeC_6N_6$. ξ_3 working down from strong to weak. Fig. 12.

I.	II.				III.
	ζ.	o_2.	ξ_3	Mean.	For mean.
$\frac{8}{160}$	3·49	—	3·38	3·44	3·07
$\frac{6}{160}$	2·49	—	2·65	2·57	3·30
$\frac{4}{160}$	2·05	—	1·78	1·92	3·42
$\frac{3 \cdot 3}{160}$	—	1·68	—	1·68	3·64
$\frac{2 \cdot \dot{6}}{160} = \frac{1}{60}$	1·49	—	—	1·49	3·99
$\frac{2 \cdot 5}{160}$	—	1·27	—	1·27	3·64
$\frac{2}{160}$	0·90	—	0·99	0·95	3·40
$\frac{1}{160}$	0·50	0 48	0·53	0·50	3 58

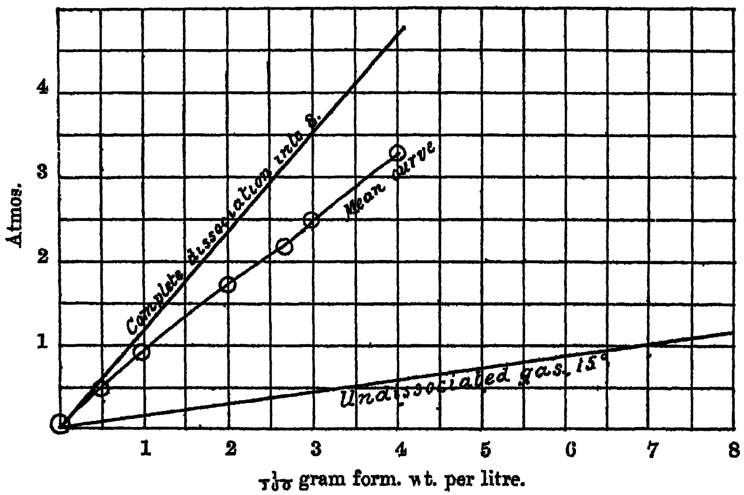
$K_4FeC_6N_6$. FIG. 12.



b. Solutions of $K_6Co_2C_{12}N_{12}$. In two pots, π_2 working down from strong to weak. Fig. 13.

	II.			III.	
I.	δ.	π_2.	Mean.	δ.	π_2.
$\frac{4}{160}$	3·46	3·28	3·37	6·19	5·85
$\frac{3}{160}$	—	2·49	2·49	—	5·95
$\frac{2\cdot\dot{6}}{160}=\frac{1}{60}$	2·17	—	2·17	5·82	—
$\frac{2}{160}$	1·77	1·70	1·74	6·35	6·08
$\frac{1}{160}$	0·91	0·90	0·91	6·50	6·43
$\frac{0\cdot5}{160}$	0·512	0·515	0·514	7·31	7·36

$K_6Co_2C_{12}N_{12}$. FIG. 13.

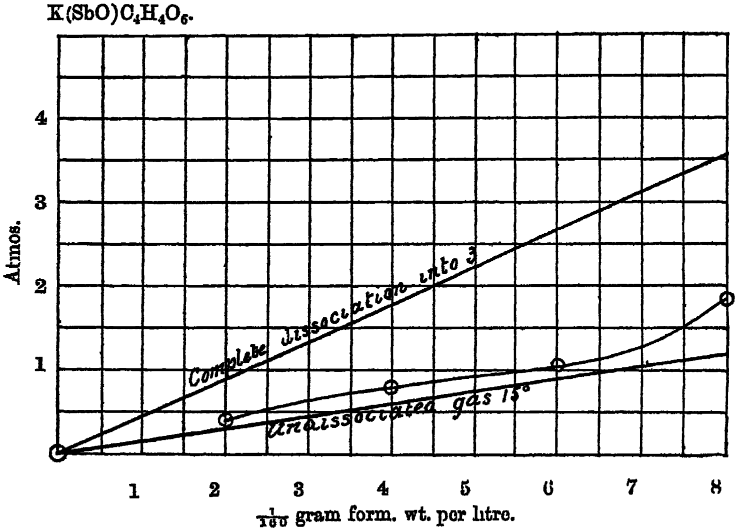


c. Solutions of $K(SbO)C_4H_4O_6$. In one pot π_2, working up from dilute to strong. Fig. 14.

I.	II.	III.
$\frac{8^1}{160}$	1·35	1·20
$\frac{6}{160}$	1·03	1·23
$\frac{4}{160}$	0·747	1·33
$\frac{2}{160}$	0·32	1·14

[1] This solution is nearly saturated.

Fig. 14.



4. *Double Salts.*

a. Solutions of $K_2Al_2(SO_4)_4,24H_2O$. In two pots, γ and ξ_1, working from strong to dilute in ξ_3. Fig. 15.

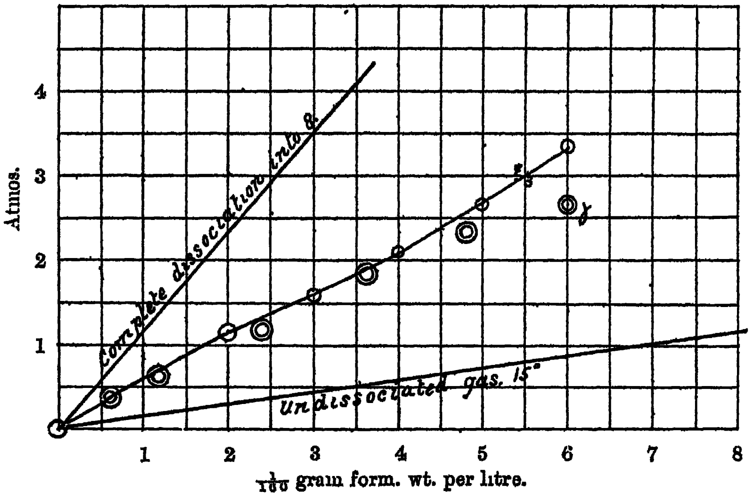
	II.		III.	
I.	γ.	ξ_3.		
$\frac{6{\cdot}023^1}{160}$	2·70	—	3 20	—
$\frac{6}{160}$	—	3·36	—	4·00
$\frac{5}{160}$	—	2·395	—	3·85

I	II.		III.	
	γ.	ξ_3.		
$\frac{4{\cdot}82}{160}$	2·32	—	3·44	—
$\frac{4}{160}$	—	2·04	—	3·65
$\frac{3{\cdot}616}{160}$	1·84	—	3·64	—
$\frac{3}{160}$	—	1·56	—	3·72
$\frac{2{\cdot}41}{160}$	1·18	—	3·50	—
$\frac{2}{160}$	—	1·08	—	3·86
$\frac{1{\cdot}205}{160}$	0·61	—	3·63	—
$\frac{1}{160}$	—	—	—	—
$\frac{0{\cdot}602}{160}$	0·37	—	4·39	—

[1] This is a nearly saturated solution.

FIG. 15.

$K_2Al_2(SO_4)_4$ 24Aq.



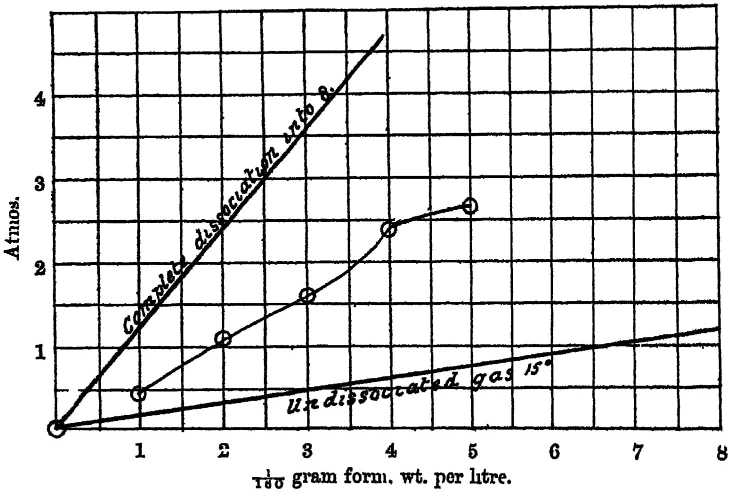
b. Solutions of $K_2Cr_2(SO_4)_4,24Aq$ in two pots. Fig. 16.

I.		II.		III.	
$\frac{5}{160}$		2·70[2]	—	3·85	—
$\frac{4}{160}$		2·46	—	4·40	—
„	Green[1]	—	2·08[3]	—	3·72
$\frac{3}{160}$		1·62	—	3·86	—
„	Green	—	1·33	—	3·17
$\frac{2}{160}$		1·10	—	3·96	—
$\frac{1}{160}$		0·47	—	3·36	—

[1] The green solution is prepared by boiling the ordinary blue-green solution, and is in a condition of dissociation, since it attacks the film.

[2] This observation may be too low, since it followed (3), which weakened the film.

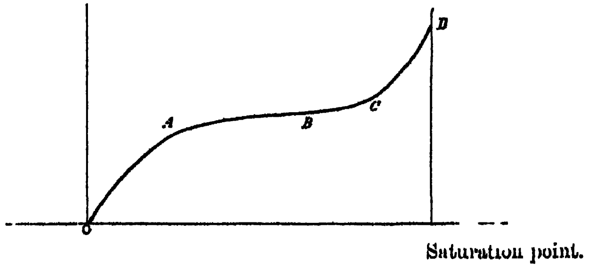
$K_2Cr_2(SO_4)_4,24Aq$. FIG. 16.



The examination of these curves leads to the observation that they are nearly continuous, and take the form OABCD, Fig. 17.

This may be divided into four parts; starting with a saturated solution at D, dilution diminishes the osmotic pressure until the point C is reached. From C to B, the curve produced passes through O, and may represent the duration of existence of some complex

FIG. 17.



molecule of the salt, or of a definite hydrate. The part CB may be long or short, and above or below the line of gaseous pressure of an undissociated molecule. At B, the specific action of the solvent may be supposed to begin dissociating this complex molecule of the salt. This goes on increasing through A towards O, but does not pass beyond the line of complete dissociation into ions. In many cases, dilution does not appear to make this part of the pressure curve approach the line of complete dissociation into ions.

The portion OABC may be well seen in the KNO_3 curve, but in the K_2SO_4 and the KI curves, only the portion OA, and a little beyond A towards B.

The portion CD is well seen at the more concentrated end of the alum, and better in the tartar emetic curve, both of which are nearly saturated.

OABC is nearly straight for KI, for the double salts, and for the salts of the compound acids.

In the case of alum, the change of direction at C takes place at the concentration $\frac{1}{100}$ gram form. wt. per litre. Where the part OA is straight, it cuts the complete dissociation line when produced backwards, at a point between $\frac{3}{800}$ and $\frac{5}{800}$ concentrations.

The presence of hydrogen in the acid salts does not appear to have any specific effect on the form of the curves.

As the curves are so nearly continuous, we cannot infer the existence of definite hydrates in the solutions of the salts examined. For this purpose, one must get a larger range of observations, which can only be procured by some less lengthy method, such as the lowering of the freezing point.

The part DC shows a loss of kinetic energy on dilution; this may be due to the retardation of the molecules in the state in which they exist in solution, being greater than that of those which are just entering the solid state.

II. *Charles' Law applied to Salts in Solution.*

In this case the difficulty is to procure a cement which will allow the formation of a film, but which will neither crack, nor melt. I found that sealing-wax joints will not allow the use of a temperature above 30°.

Using the sodiophosphate of zinc, I have got one observation. Unfortunately, the solution used, potassium ferrocyanide, attacked the film at a temperature of 70°, and I have not been able to get another film.

At 17°, $\frac{2\cdot5}{160}$ $K_4FeC_6N_6$ gave a pressure of 0·77 atmo.

54° „ „ „ „ 1·13 „

Assuming Charles' law applies to salts in solution, and that $K_4FeC_6N_6$ behaves as a single unit, the pressure should have been

$$\frac{0\cdot77 \times 327}{290} = 0\cdot87 \text{ atmo.}$$

That is, the calculated rise on this assumption

$$= 0\cdot87 - 0\cdot77 = 0\cdot10 \text{ atmo.}$$

But the observed rise

$$= 1\cdot13 - 0\cdot77 = 0\cdot36 \text{ atmo.}$$

Now, on reference to the preceding results, I, 3, *a*, we find that the ratio of observed osmotic pressure to that calculated on the undissociated molecule hypothesis is about 3·65* for the above solution. Therefore, the calculated rise, instead of being 0·10 atmo., should be 0·10 — 3·65 = 0·365 atmo., which is the value found.

That is, so far as a single experiment can uphold the point, Charles' law does appear to apply to salts in solution.

It must be noted that the factor *i*, whatever be its interpretation, appears here as well as in the application of Boyle's law.

III. *Dalton's Law of Partial Pressures applied to Salts in Solution.*

I have arranged the values obtained under three heads:—

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* The factor, 3·65 is that found for the above solution at 17°. De Vries has shown (*loc. cit.*) that the ratios of *i* are nearly independent of temperature.

a. Salts which combine to form well-marked double salts :—

	In pot *κ*.		In pot *τ*.	
Salt solution.	Osmotic pressure	Sum of components	Osmotic pressure	Sum of components.
$\frac{1}{10}(NH_4)_2SO_4$	1·264	—	1·295	—
$\frac{1}{40}Al_2(SO_4)_3$	1·265	—	1·22	—
$\frac{1}{40}K_2SO_4$	1·29	—	1·40	--
$\frac{1}{40}(NH_4)_2Al_2(SO_4)_4,24Aq$	2·37	2·53	1·98	2·515
$\frac{1}{40}K_2Al_2(SO_4)_4,24Aq$....	2·39	2·56	1·96	2·32

b. Salts of the same acids, which do not form double salts :—

i. Iodides in pot o_2 :—

Salt solution.	Osmotic pressure.	Sum of components.
$\frac{1}{40}KI$	0·92	—
$\frac{1}{80}CaI_2$	0·65	—
$\frac{1}{40}KI + \frac{1}{80}CaI_2$	1·83	1·57

ii. Sulphates in pot o_2 :—

Salt solution.	Osmotic pressure.	Sum of components.
$\frac{0·574}{40}CaSO_4$	0·467	—
$\frac{1}{40}K_2SO_4$..............	1·43	-
$\frac{0·574}{40}CaSO_4 + \frac{1}{40}K_2SO_4$	1·88	1·897

c. Salts of different acids which do not form double salts :—

Salt solution.	In pot τ. Osmotic pressure.	In pot τ. Sum of components.	In pot o_2. Osmotic pressure.	In pot o_2. Sum of components.
$\frac{1}{40}K_2SO_4$	1·40	—	1·43	—
$\frac{1}{40}KNO_3$	0·814	—	0 96	—
$\frac{1}{160}K_4Fe(CN)_6$	0·50	—	0·48	—
$\frac{1}{40}K_2SO_4 + \frac{1}{40}KNO_3$	2·05	2·21	2·37	2·39
$\frac{1}{40}K_2SO_4 + \frac{1}{160}K_4Fe(CN)_6$	1·80	1·90	1·935	1·91
$\frac{1}{40}KNO_3 + \frac{1}{160}K_4Fe(CN)_6$	1·23	1·31	1·495	1·44

As a whole, these results show that when the two components can combine to form a double salt, Dalton's law does not hold accurately, and that the observed pressure for the compound is less than the sum of the pressures of the constituents.

In the cases when the components do not combine to form a double salt which may be crystallised out, the observed pressure of the mixture of the two salts is about equal to the sum of the pressures of the constituents. In the case of the iodides, *b*, i, the observed pressure is even considerably greater than the sum. In the results of pot τ in *c*, as in those of pot o_2 in the same class, the deviations, when in the same direction, are smaller than those in class *a*.

IV. *Influence of the Acid.*

a. Solutions of potassium salts of different strengths, mostly in one pot δ:—

	$\frac{1}{20}$		$\frac{1}{40}$		$\frac{1}{60}$		$\frac{1}{80}$	
	o. p.	*i.*	o. p.	*i.*	o. p.	*i.*	o. p.	*i.*
KNO_3	1·64	1·47	0·96	1·72	—	—	0·47	1·66
KI	1·81	1·62	0·92	1·64	—	—	0·496	1·77
$KClO_3$	1·73	1·55	—	—	—	—	—	—
$KC_2H_3O_2$	1·26	1·13	—	—	—	—	—	—
K_2SO_4	2·16	1·93	1·25	2·24	—	—	—	—
$K_2C_2O_4$	2·26	2·02	1·31	2·34	—	—	—	—
$KHCO_3$	1·32	1·18	0·66	1·17	—	—	—	—
$KHSO_3$	—	—	0·79	1·41	—	—	—	—
$K_2C_4H_4O_6$	2·30	2·50	1·17	2·10	—	—	—	—
$K(SbO)C_4H_4O_6$	1·35	1·21	0·75	1·34	—	—	0·32	1·14
$K_4Fe(CN)_6$	3·49	3·12	2·05	3·67	1·49	4·11	0·90	3·14
$K_6Co_2(CN)_{12}$	—	—	3·46	6·18	2·17	5·98	1·77	6·35

b. Solutions of sodium salts of different strengths, mostly in δ :—

	$\frac{1}{20}$		$\frac{1}{40}$		$\frac{1}{60}$	
	o. p.	*i*.	o. p.	*i*.	o. p.	*i*.
$NaNO_3$	1·59	1·42	—	—	—	—
$Na_2S_2O_3$....	2·21	1·95	1·30	2·33	—	—
Na_2HPO_4 ..	1·82	1·63	1·50	2·68	0·51	1·42
Na_3Ci......	—	—	—	—	0·97	2·68

c. Solutions of potassium salts of organic acids. Two series in pots ρ_2 and τ for $\frac{1}{20}$ form. wt. per litre :—

	ρ_2.		τ.	
	o. p.	*i*.	o. p.	*i*.
KFo...........	1·09	0·975	1·43	1·28
KAc	1·42	1·27	1·66	1·48
KPr...........	1·46	1·33	1 78	1·59
KBz	1·95	1·74	—	—
K_2Ox..........	2·26 (δ)	2·02	—	—
$\frac{1}{40}$ K_2Ox...........................			1·41 1·41 1·31	2·52

These results are discussed after the next series.

V. *Influence of Base.*

a. Solutions of nitrates of different bases in two pots, η and β :—

	$\frac{1}{20}$			$\frac{1}{40}$		
	η.	β.	*i*.	η.	β.	*i*.
KNO_3......	1·61	1·76	1·50 (Mean)	0·89 (Mean)	—	1·59
$NaNO_3$.....	—	1·79	1·60	0·60	—	1·07
NH_4NO_3 ...	—	1·48	1·32	0·66	—	1·18
$Mg(NO_3)_2$..	2·12	—	1·89	0·96	—	1·72
$Ca(NO_3)_2$...	1·67	—	1·49	1·07	1·08	1·92 (Mean)
$Sr(NO_3)_2$...	1·58	—	1·41	—	1·38	2·47
$Ba(NO_3)_2$ ..	—	2·04	1·82	—	1·33	2·38
$Co(NO_3)_2$ ..	2·14	—	1·91	1·35	—	2·12
$Cu(NO_3)_2$ ..	2·14	—	1·93	0·93	—	1·66

b. Solutions of sulphates of different bases in two pots, κ and τ, with O.P. for $\frac{1}{20}$ in different pots :—

	$\frac{1}{20}$		$\frac{1}{40}$		
	o p.	*i.*	κ.	τ.	*i* for mean.
K_2SO_4	2·19	1·97	1 29	1·40	2·40
Na_2SO_4	3·13	2·79	—	—	—
$(NH_4)_2SO_4$	2·64	2·38	1·26	1·295	2·29
$MgSO_4$	0·78[1]	0·70	—	—	—
$CaSO_4$	—	—	0·79[2]		1·41
$Al_2(SO_4)_3$	—	—	1·265	1·22	2·23

[1] Probably due to destruction of film by the salt.

[2] Extrapolation value beyond saturated solution, and has no interpretation. Inserted to show different order of O.P. for an undissociated solution.

c. Solutions of alums of different composition of $\frac{1}{10}$ gram form. wt. per litre; κ at 16°, τ at 14°:—

	O. p.		*i.*	
	κ.	τ.	κ.	τ.
$K_2Al_2(SO_4)_4,24H_2O$	2·39	1·96	4·27	3·50
$K_2Cr_2(SO_4)_4,24H_2O$	2·46	—	4·40	—
$(NH_4)_2Al_2(SO_4)_4,24H_2O$	2·37	1·98	2·25	3·54

d. Solutions of normal and hydrogen salts :—

$\frac{1}{40}$ Na_3Ci............ [1·46 calcd.] $\frac{1}{60} = 0·97$.

$\frac{1}{40}$ Na_2HCi.......... 2·12

$\frac{1}{40}$ K_2Ox............ 1·41

$\frac{1}{40}$ $KHOx$.......... 0·77

Na_3PO_4, $KHSO_4$, and K_2SO_3 are decomposed by water, and dissolve the film.

Magnesium, copper, ammonium and sodium nitrates, and ammonium sulphate have smaller values of *i* for dilute solutions than for concentrated. This may be explained by the existence of a hydrate, but it is not practicable to define them, by this method.

In examining these results, it must be remembered that they are taken at any points in the curve OABCD, § I. In order to be strictly comparable they should be taken from OA, or from BC; this is confirmed by the fact that the values of *i* are more nearly constant for $\frac{1}{20}$ than for $\frac{1}{10}$ solutions in the case of the bases, and that this point is in BC.

It must be noted that sodium salts generally are more dissociated than potassium salts, particularly when the acids have high affinity. This is also borne out by the fact that sodium salts generally destroy the film, sooner or later, whilst potassium salts do not. The sulphates also are much more dissociated in watery solution than the nitrates, except when they form double salts, such as the alums.

The base values do not appear to be periodic, but rather to be connected with the acidity of the base.

No general principle governs the action of hydrogen in acid salts; in some cases it lowers the O.P., in others it raises it.

Taking the salts of the organic acids first, we see that an increase in the molecular weight of the acids is accompanied by an increase of the O.P., and also that the O.P. seems to depend on the basicity of the acid.

This may be interpreted that the carboxyl group gradually loses its unsaturated condition with increase of molecular weight of the attached carbon group, so that the retardation which occurs from the action of the water on the carboxyl group gradually loses its prominence.

In order to compare my values of osmotic pressures with those of the electric conductivities, I append the following values of Kohlrausch's (*B.A. Reports*) for the molecular conductivities of solutions of $\frac{1}{10}$ gram form. wt. per litre ($= 10^8\,k/m$, where $k =$ the conductivity and $m =$ the molecule in grams). The osmotic pressures are those determined for $\frac{1}{20}$ gram form. wt. per litre.

	Kohlrausch.		o. p.
KNO_3	983		1·64
KI	1069		1·81
$KClO_3$	927		1·73
KAc	784		1·26
$\frac{1}{2}K_2SO_4$	897	$\frac{1}{40}$	1·25
KNO_3	983		1·76
$NaNO_3$	817		1·79
$\frac{1}{2}Ba(NO_3)_2$	755	$\frac{1}{40}$	1·33
$\frac{1}{2}K_2SO_4$	897	$\frac{1}{20}$	2·19
$\frac{1}{2}Na_2SO_4$	734	$\frac{1}{20}$	3·13

The values in the two cases appear to take a similar direction, though in the case of sodium, my values are always higher than the corresponding values for potassium.

Kohlrausch also gives the relative velocities of the ions:—

K.	NH_4.	Na.	H.	$\frac{1}{2}$Ba.	$\frac{1}{2}$Mg.
62	50	32	274	30	26

I.	NO_3.	ClO_3.	Ac.
55	48	44	26

These velocities take the same direction as the osmotic pressure values, except in the case of sodium. This might be expected if osmotic pressure and electric conductivity are due to the same cause, since the O.P. must depend on the velocity as well as the mass of the molecule.

I append the values of the relative affinities of the acids used, from Ostwald.

HCl	1·00
HI	0·97
HNO_3	0·96
$HClO_3$	0·96
H_2SO_4	0·73
HF	0·016
HAc	0·004
HPr	0·003
H_2Ox	0·18
H_2T	0·023
H_3Ci	0·017

He states that no base affinity tables have been constructed which have any value.

It will be seen that for the inorganic acids a high relative affinity is accompanied by a high O.P. of their salts, whilst in the case of the organic acids, the reverse holds. I think this must conclusively prove that there is some other factor entering into the problem of solution besides simple dissociation into ions.

VI. *Avogadro's Law applied to Salts in Solution.*

In comparing the results obtained, and looking at the values of P/π or i, it will be seen that it is always greater than unity or approximately equal to it. Its excess above unity tends, except for nearly saturated solutions, to increase with increasing dilution. (See remarks on I.)

In the table in IV, the values of i vary much. For $\frac{1}{20}$ form. wt.

per litre the limits are 1·13 to 2·02 for simple salts, and for $\frac{1}{10}$ form. wt. 1·17 to 2·34.

In the table in V, the values of *i* do not differ so much: 1·33—1·93 for $\frac{1}{20}$ form. wt. per litre, and 1·66—2·47 for $\frac{1}{10}$.

This confirms the fact that the osmotic pressures do not furnish any guide to the determination of the molecular weights of inorganic salts in solution in water, at least for comparison with gaseous molecular weights. It is possible that the results may be more consistent with organic than with metallic bases.

In the case of the acids, the osmotic pressures of the solutions which contain $\frac{1}{20}$ equivalent of potassium, or sodium per litre agree much better than the corresponding proportion of the formula weight.

The sulphates are more consistent than the nitrates, though they dissociate more easily; the latter may be connected with the formation of water compounds of the acid formed by dissociation, giving as result a basic salt in solution, mixed with dilute sulphuric acid.

The limiting value of *i*, as found by Arrhenius' hypothesis into ions is as follows—

$$\text{For}\quad \begin{array}{ll} M'X' \ \ldots\ldots\ldots\ldots\ldots & = 2 \\ M''X'_2 \text{ or } M'_2X'' \ \ldots\ldots & = 3 \\ \left\{\begin{array}{c} M'''X'_3 \text{ or } M'_3X''' \\ \text{or } M''_2X'_2 \end{array}\right\} \ \ldots & = 4 \end{array}$$

where M = any metal,

X = any acid radicle.

These values are not exceeded in my observations, and it is only the stronger acids and bases which approach this limit. On the other hand, for the organic acids, the stronger are less dissociated.

If dissociation into ions takes place, why do they not get through the film rather than the water molecules? As a matter of fact, the dissociations which can be observed are those of the salt into an acid and a basic portion, of which the acid part gets through, and destroys the film. This passage of the ions through the film should be more distinctly noticeable in the case of the acid salts, where, according to Kohlrausch's numbers, the velocity of H is 274; while that of K is only 62. However we do not find the O.P. of these salts less than it ought to be, from this cause, V, *d*.

On the other hand, the value of *i* may be conditioned by the amount of dissociation of the molecules of the salt, produced by the action of the solvent, as described above. On this hypothesis, the value of *i* at its limit represents the maximum amount of dissociation of each molecule of the solid in the state in which it exists in solution, produced by the action of the solvent.

There is no doubt that the values of *i*, obtained by any of the various methods in use, agree with one another, are fairly definite, and have a meaning, but I incline to the explanation that the action of the solvent is twofold, and may be expressed as—

i. Combination of the molecules of the dissolved substance with the solvent to form complex molecules.

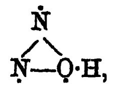
ii. Separation of the complex molecules of the dissolved substance, under the action of the solvent, into simpler molecules, not necessarily as small as the limiting gaseous molecule.

In conclusion, I have great pleasure in thanking Professor J. J. Thomson for the use of the Cavendish Laboratory, Cambridge, where this research was conducted, and for his kind assistance, and advice during the progress of the work.

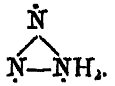
XLII.—*Notes on the Azo-derivatives of β-Naphthylamine.*

By Raphael Meldola, F.R.S., and Frank Hughes.

At the beginning of the present session we commenced an investigation having for its object the extension of the results which had previously been arrived at respecting the constitution of the azo-derivatives of β-naphthol by one of the authors in conjunction with F. J. East (Trans., 53, 1888, 460) and Gilbert T. Morgan (Trans., 55, 1889, 114 and 603). The work was carried on till one of us (F. H.) received an appointment necessitating removal from London, and although we cannot regard the present communication as throwing any new light on the question of the constitution of the azo-derivatives of β-naphthylamine, we have been able to obtain a sufficient number of new derivatives of these compounds to warrant our submitting a description of them to the Society. The conclusion to which the former researches on the perfectly analogous compounds of β-naphthol have led is that the atom of hydrogen, which in these compounds is replaceable by alkyl and alkoyl radicles, is attached to oxygen, and that the quinonoid formula of the azo-β-naphthol derivatives is accordingly rendered improbable. It has been suggested by one of us (R. M.) that these last compounds contain the group



and analogy would therefore lead to a similar formula for the compounds derived from β-naphthylamine, viz., that the latter contain the group



Much evidence has been adduced in favour of the view that these compounds contain the NH_2 group, and is so well known that it need not be recapitulated here; but that this evidence still appears insufficient to some chemists is shown by the fact that in a paper published last year by H. Goldschmidt and G. Rosell (*Ber.*, **23**, 1890, 487) the quinonoid formula is adopted by these authors both for the β-naphthol and β-naphthylamine azo-derivatives. It is for the purpose of obtaining further evidence as to whether these last compounds contain two hydrogen atoms attached to the same nitrogen atom that the present experiments have been commenced. As in the previous part of the work on the azo-β-naphthol derivatives the most satisfactory results were obtained when the aromatic nucleus linked by the azo-group to the naphthalene residue contained a strongly acid radicle (NO_2), it was thought desirable to begin with the analogous nitroazo-compounds of β-naphthylamine, the more especially as the simpler benzeneazo-β-naphthylamine has already been made the subject of numerous experimental investigations by Zincke and Lawson, Goldschmidt, &c.

Orthonitrobenzeneazo-β-naphthylamine.

Para- and meta-nitrobenzeneazo-β-naphthylamine were described by one of us many years ago (Trans., 1883, **43**, 430; and 1884, **45**, 116). In order to complete the series of isomerides, we have now prepared the isomeric compound from diazotised orthonitraniline and β-naphthylamine. The orthonitraniline was diazotised in the usual way with the calculated quantity of sodium nitrite in hydrochloric acid solution, and the diazo-chloride poured into the cold, dilute aqueous solution of β-naphthylamine hydrochloride. The azo-compound at once separates as a dull, bronzy powder, and after being collected and washed well with water, it was crystallised from alcohol and finally from glacial acetic acid until the analysis showed that the substance was pure. The following results were obtained:—

I. 0·1233 gram gave 0·2987 gram CO_2 and 0·0568 gram H_2O.
II. 0·1619 „ „ 0·3904 „ „ 0·0726 „ „
III. 0·0991 „ „ 16 c.c. moist N at 9° and 757·8 mm. bar.
IV. 0·1574 „ „ 25·8 c.c. moist N at 11·5° and 752·6 mm bar.

	Calculated for $C_{10}H_6{<}\genfrac{}{}{0pt}{}{N_2\cdot C_6H_4\cdot NO_2}{NH_2}$.	Found.			
		I.*	II.	III.	IV.
C	65·75	66·07	65·76	—	—
H	4·11	5·11	4·98	—	—
N	19·18	—	—	19·33	19·21

The pure substance forms lustrous, bronzy scales melting sharply at 198°. It is soluble in alcohol and benzene, but more readily in boiling glacial acetic acid. All the solutions are orange-red. Strong sulphuric acid dissolves it with a deep indigo-blue colour, which changes to red on dilution and then again to blue as the substance is precipitated in a finely-divided form.

One striking character of the compound is its close resemblance in general appearance to the isomeride from paranitraniline, these two modifications presenting a marked contrast in colour to the brilliant orange needles of metanitrobenzeneazo β-naphthylamine. Unlike the paranitro-compound, however, it does not appear to be reducible in alcoholic solution with ammonium sulphide.

Action of Nitrous Acid in the presence of Acetic Acid.—Three grams of the substance were dissolved in 110 c.c. of hot glacial acetic acid, and when the solution had cooled to 70°, 1 mol. proportion of solid sodium nitrite was added in small portions. The deep, reddish-orange solution became lighter, and was allowed to stand till quite cold. On diluting with water, a precipitate consisting of orange needles separated; this proved to be orthonitrobenzeneazo-β-naphthol. Under the same conditions, therefore, that the meta- and paranitro-compounds form azonaphthyl-acetates (Trans., 1888, **53**, 460),† the orthonitro-compound passes directly into the corresponding azo-β-naphthol. The latter, prepared as described, was purified by crystallising it several times from hot glacial acetic acid, and was finally obtained in the form of bright, orange-red needles melting at 209—210°:—

0·1196 gram gave 0·2866 gram CO_2 and 0·0427 gram H_2O.
0·1348 „ 16 c.c. moist N at 10° and 752·8 mm. bar.

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* The high results for the hydrogen are attributable to the oxides of nitrogen, the formation of which was most difficult to avoid, and impossible to prevent entirely.

† I should like to take the present opportunity of correcting an error which appears in the title of a note on this reaction, which was communicated to the *Berichte* at the time of its discovery. The note, written in English, bore the title "Replacement of the Amido-group by the Acetoxy-group [meaning of course $-O\cdot C_2H_3O$] by means of the Diazo-reaction." The translator rendered this, "Ueber den Ersatz der Amidogruppe durch die Acetylgruppe mit Hulfe der Diazoreaction" (*Ber.*, 1888, 21, 601). The contents of the note fortunately convey their own refutation of the title, but the inconsistency nevertheless requires clearing up.—R. M.

	Calculated for $C_{10}H_6<^{N_2\cdot C_6H_4\cdot NO_2}_{OH}$.	Found.
C	65·53	65·35
H	3·75	3·97
N	14·34	14·05

Orthonitrobenzeneazo-β-naphthol is only sparingly soluble in alcohol, but more readily in boiling glacial acetic acid. Like all the azo-derivatives of β-naphthol, it is devoid of phenolic characters, being quite insoluble in hot aqueous caustic soda. It dissolves in hot alcoholic soda with a claret-red colour. Strong sulphuric acid dissolves it with a violet colour, which becomes orange on dilution with water, the unaltered compound being thereby precipitated.

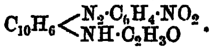
In order to see whether the amido-group of the β-naphthylamine azo-compound could be displaced by the acetoxy-group at a lower temperature, a cold, saturated solution of the substance in glacial acetic acid was treated as before with the necessary quantity of sodium nitrite. After standing for some hours, the solution was diluted with water, when a deep-red oil gradually settled down. This oil did not solidify on standing, and it was therefore washed with water and at once hydrolysed by boiling with alcoholic potash. The product, after being crystallised from glacial acetic acid, was identified as orthonitrobenzeneazo-β-naphthol (m. p. 209—210°), thus showing the red oil to have been orthonitrobenzeneazo-β-naphthyl acetate.

Acetyl Derivatives of the Nitrobenzeneazo-β-naphthylamines.

As a preliminary step towards the solution of the problem whether there are in the orthamidoazo-compounds two replaceable hydrogen atoms attached to the same nitrogen atom, it seemed advisable to prepare some of the derivatives containing acid radicles. It has already been pointed out by Lawson (*Ber.*, 1885, 18, 796) that benzeneazo-β-naphthylamine forms an acetyl and a benzoyl derivative. We have prepared the acetyl derivatives of the nitroazo-compounds obtained from the three nitranilines and β-naphthylamine. There is a great tendency for the decomposition to proceed too far during acetylation, and care must be taken to avoid too high a temperature; if this precaution is not observed, resinous products are formed. After several preliminary trials, the acetyl derivative of paranitrobenzeneazo-β-naphthylamine was prepared in the following way:—

The substance was placed in a dry flask and sufficient acetic anhydride added just to cover it; the flask was then heated in boiling water for about 15 minutes, the contents diluted with water, and the crude acetyl derivative collected and washed. After several crystallisations from glacial acetic acid, the substance was obtained pure in the form of brick-red needles melting at 227—228°.

0·1245 gram gave 0·2950 gram CO_2 and 0·0517 gram H_2O.
0·1384 „ 19·5 c.c. moist N at 11° and 752·5 mm. bar.

	Calculated for  $C_{10}H_6<\begin{matrix}N_2\cdot C_6H_4\cdot NO_2\\ NH\cdot C_2H_3O\end{matrix}$.	Found.
C	64·67	64·62
H	4·19	4·61
N	16·76	16·61

This acetyl derivative is very insoluble in alcohol, but readily soluble in benzene, the solution being of an orange colour. It dissolves in cold strong sulphuric acid with a reddish-violet colour, and on diluting with water this passes into a yellow, the solution remaining clear for some time. Whether this change indicates the formation of a sulphonic acid or some deeper structural modification is a point requiring further investigation. It was thought not improbable that by appropriate treatment the hydrogen atom of the acetamido-group might be replaced by the nitroso-group, but we have not succeeded in preparing a nitroso-derivative. By the action of sodium nitrite on a cold solution of the substance in glacial acetic acid, the unaltered compound is simply "salted out" in a crystalline form. The acetyl derivative dissolves in cold, strong nitric acid (sp. gr. 1·42) forming a red solution. On pouring the latter into a large volume of cold water, a bulky and almost gelatinous orange precipitate slowly separates. The very different appearance of this precipitate, as compared with the original compound, led us at first to the belief that substitution had taken place, but the precipitate gradually became red on standing, and the melting point and analysis of the product proved that it was unchanged. The alteration of colour may indicate simply a change from a colloïdal to a crystalline state, or the decomposition by water of an unstable compound formed with the acid. Even fuming nitric acid appears to be without action on the compound in the cold; by heating with an acid of this strength (1·5 sp. gr.) for an hour and then pouring the cold solution into water, a reddish substance was obtained, which, when washed and dried, was extremely insoluble in all the ordinary solvents, and could only be obtained in a crystalline condition by dissolving in hot nitrobenzene and precipitating by the gradual addition of alcohol. The substance was thus obtained in the form of a microcrystalline, red powder, which was collected, washed with alcohol, and dried. It had no definite melting point, but commenced to blacken and decompose about 236°. Analysis gave the result:—

0·1164 gram gave 17·8 c.c. moist N at 11° and 755 mm. bar.

This agrees fairly well with the formula of a mononitro-derivative. Calculated percentage of N = 18·47; found 18·09.

The acetyl derivative of metanitrobenzeneazo-β-naphthylamine was prepared in the same way as the foregoing. A portion of the crude product was crystallised from boiling glacial acetic acid, but as this treatment gave indications of decomposition, with the formation of resin (probably owing to the high temperature of the boiling acid), this solvent was abandoned and the remainder of the substance was purified by crystallisation from alcohol till a constant melting point indicated the purity of the preparation:—

0·1568 gram gave 0·3736 gram CO_2 and 0·0613 gram H_2O.
0·1630 „ 23·1 c.c. moist N at 13° and 760·4 mm. bar.

	Calculated.	Found.
C	64·67	64·98
H	4·19	4·34
N	16·76	16·74

The pure substance forms bright orange needles melting at 192°; it is very sparingly soluble in alcohol, more readily in benzene. Strong sulphuric acid dissolves it with a violet colour, which becomes yellow on dilution with water.

Orthonitrobenzeneazo-β-naphthylamine was acetylated in a different way from the other compounds, namely, by heating the glacial acetic acid solution just to the boiling point with the theoretical quantity of acetic anhydride for about 15 minutes. On cooling, the acetyl derivative separates in the form of dull orange needles. The compound was purified by successive crystallisations from alcohol, and then formed orange-brown needles melting at 154°:—

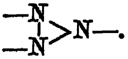
0·1811 gram gave 0·4305 gram CO_2 and 0·0700 gram H_2O.
0·1438 „ 20·3 c.c. moist N at 11° and 764·3 mm. bar.

	Calculated.	Found.
C	64·67	64·82
H	4·19	4·29
N	16·76	16·93

The substance is very similar in properties to the other acetyl derivatives, dissolving in strong sulphuric acid with a violet colour, which becomes orange-yellow on dilution with water.

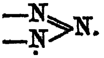
Pseudazimides from Nitroazo-derivatives of β-Naphthylamine.

In 1885, Zincke made the interesting discovery (*Ber.*, 1885, **18**, 3132) that the azo-derivatives of β-naphthylamine lost two atoms of hydrogen on oxidation, and were converted into colourless compounds, which were regarded as related to Griess's azimido-compounds (*Ber.*, 1882, **15**, 1878). According to this view they contain the group



$$\begin{array}{l}-N\\ \;\;|\;\;>N-.\\ -N\end{array}$$

It has been since shown by several investigators (see *Phil. Mag.*, 1887, 525; Noelting and Abt, *Ber.*, 1887, **20**, 2999; Zincke and Lawson, *Annalen*, **240**, 110; Zincke and Arzberger, *ibid.*, **249**, 350; Zincke and Campbell, *ibid.*, **255**, 339) that the azimides of Griess really belong to an isomeric series, and for the compounds produced by the oxidation of orthoamidoazo-compounds, Zincke has proposed the name of "pseudazimides," the latter containing the group of nitrogen atoms above formulated, whilst the azimides of Griess contain the asymmetric group



$$\begin{array}{l}-N\\ \quad\;\;>N.\\ -N\end{array}$$

In order to prepare the pseudazimides from the azo-β-naphthylamine derivatives forming the subject of the present communication, Zincke's method of oxidation was resorted to. Five grams of paranitrobenzeneazo-β-naphthylamine were dissolved in 400 c.c. of hot glacial acetic acid, and a strong aqueous solution of chromic acid was added in small portions till the colour of the solution had disappeared. The contents of the flask were cooled whenever the evolution of nitrogen indicated that the temperature was getting too high. In a properly conducted experiment, there should be no escape of nitrogen. When a sufficient quantity of chromic acid has been added, the deep orange-red of the original solution changes to a light greenish-yellow, and on diluting with water and allowing to stand for a day, the crude product separates as a light ochreous powder. The latter was collected, washed with water, dried, and purified by crystallisation, first from glacial acetic acid and then from toluene. The crude substance is very impure, and requires several crystallisations before the melting point is constant. The yield is not very good, as resinous byeproducts are formed during the oxidation. Analysis of the purified substance gave the results:—

I.	0·1851 gram	gave	0·4499 gram CO_2	and	0·0601 gram H_2O.
II.	0·1321	„	0·3198 „	„	0·0425 „
III.	0·0931	„	15·6 c.c. moist N at 14·5° and 741 mm. bar.		
IV.	0·1233	„	20·5 c.c. moist N at 13° and 758·7 mm. bar.		

These numbers agree with those required by the formula of the pseudazimide,

$C_{10}H_6<\overset{N}{\underset{N}{|}}>N\cdot C_6H_4\cdot NO_2(p)$.

	Calculated for $C_{16}H_{10}N_4O_2$.	Found.			
		I.	II.	III.	IV.
C	66·21	66·29	66·03	—	—
H	3·45	3·61	3·57	—	—
N	19·34	—	—	19·14	19·59

The pure compound forms flat, transparent, whitish needles melting at 236°, and softening a few degrees lower. It is quite devoid of basic properties, and is very sparingly soluble in alcohol, acetic acid, and toluene. On reduction, it appears to give rise to a non-basic, insoluble compound which has not yet been investigated.

The corresponding pseudazimide from metanitrobenzeneazo-β-naphthylamine was prepared in precisely the same way as the foregoing compound. After crystallisation from acetic acid and toluene alternately, it forms opaque, whitish needles melting at 223—224°.

0·2145 gram gave 0·5199 gram CO_2 and 0·0694 gram H_2O.
0·0958 „ 15·7 c.c. moist N at 14° and 771·4 mm. bar.

	Calculated.	Found.
C.............	66·21	66·10
H	·3·45	3·59
N	19·34	19·49

The yield is somewhat better than in the case of the isomeric paranitro-compound, and the substance is more soluble in the ordinary solvents used for its purification. We have not as yet been enabled to obtain a basic derivative from it by reduction.

Orthonitrobenzeneazo-β-naphthylamine, on oxidation with chromic acid, also gives a pseudazimide, but the yield is small, and so much resinous impurity is produced that we have not further investigated this reaction.

Action of Nitric Acid on Azo-β-naphthylamine Derivatives.

We have commenced a preliminary study of the action of nitric acid on the above-named compounds, but have not yet obtained any information concerning the nature of the products, as the latter are apparently uncrystallisable, and are all more or less explosive. Some definite change takes place, however, under the influence of this reagent, and the investigation will be resumed. The results thus far obtained are as follows:—

Paranitrobenzeneazo-β-naphthylamine was added in small portions to well-cooled fuming nitric acid (1·5 sp. gr.). The substance dissolves at once without evolution of gas, and with the formation of an orange solution. The latter was allowed to stand in the cold for some hours, and was then poured into a large volume of cold water, when an orange, flocculent substance was thrown out. The latter was collected, washed with water, then with alcohol, in which it is but very slightly soluble, and finally allowed to dry in the air. It could not be crystallised from any solvent. A specimen was purified by dissolving in nitrobenzene and precipitating by alcohol. An amorphous, orange powder was thus obtained, which, when collected, washed with alcohol, and dried in the air, gave the following results:—

0·1918 gram gave 29·5 c.c. moist N at 11° C. and 770·8 mm. bar. = 18·58 per cent. N.

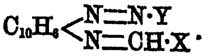
0·1084 gram gave 16·6 c.c. moist N at 10·5° C. and 770·5 mm. bar. = 18·53 per cent. N.

These numbers do not agree with the formula of a mononitro-derivative (requiring 20·77 per cent. N), but rather with that of the unaltered compound (requiring 19·18 per cent. N). The substance begins to shrink at 90°, and at 109° decomposition begins to set in. If heated suddenly to this temperature, it deflagrates.

Benzeneazo-β-naphthylamine is acted upon by fuming nitric acid in like manner to the foregoing. The product is very similar in appearance and properties, and is also explosive (decomposing point about 115°). The percentage of nitrogen in the crude substance agrees also more closely with that in the unaltered compound than with a nitro-derivative (calculated for unaltered compound, N = 17 per cent.; for mononitro-derivative, 19·2; found 16·74 and 17·62). Although these nitrated products have not yet been obtained in a state of purity, they seem sufficiently definite to warrant an extension of the work in this direction, and an examination of their products of reduction may perhaps throw some light on their nature.

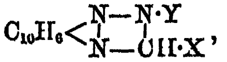
Action of Aldehydes on the Azo-derivatives of β-Naphthylamine.

If β-naphthylamine is acted upon by an aldehyde so as to obtain the condensation product of the general formula $C_{10}H_7N{:}CH{\cdot}X$, the latter readily combines with diazotised aniline, nitranilines, &c., to form scarlet, resinous azo-compounds of the type



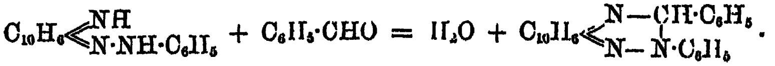
$$C_{10}H_6<\begin{matrix}N{=}N{\cdot}Y\\ N{=}CH{\cdot}X\end{matrix}\cdot$$

These readily pass into the corresponding triazines,

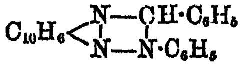
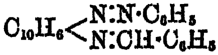


$$C_{10}H_6<\begin{matrix}N-N\cdot Y\\ | \quad\ \ | \\ N-CH\cdot X\end{matrix},$$

on heating with acid (Meldola, Trans., 57, 1890, 328). If, instead of starting with the condensation product of β-naphthylamine and the aldehyde, the azo-derivative of β-naphthylamine is first prepared, and then the latter heated with the aldehyde, the triazine is at once formed. This method was discovered independently by one of the authors, and by Goldschmidt and Rosell (*Ber.*, 23, 1890, 505), and many of the triazines have been prepared in this way, and will form the subject of a future communication. In the present state of the work, the most important point appears to be the bearing of the reaction on the question of the constitution of the orthamidoazo-compounds. The investigators named represent the action of benzaldehyde on benzeneazo-β-naphthylamine by the equation



$$C_{10}H_6<\begin{matrix}NH\\ N\cdot NH\cdot C_6H_5\end{matrix} + C_6H_5\cdot CHO = H_2O + C_{10}H_6<\begin{matrix}N-CH\cdot C_6H_5\\ | \qquad | \\ N-N\cdot C_6H_5\end{matrix}.$$

They give the alternative formula  $C_{10}H_6<\begin{matrix}N-CH\cdot C_6H_5\\ | \qquad | \\ N-N\cdot C_6H_5\end{matrix}$ for the triazine. The same triazine can, however, be prepared from the azo-compound,  $C_{10}H_6<\begin{matrix}N{:}N\cdot C_6H_5\\ N{:}CH\cdot C_6H_5\end{matrix}$ (Trans., 57, 1890, 328), and as the benzylidene-β-naphthylamine which is used as the starting point in this process, is unquestionably derived from a compound containing the NH_2 group (β-naphthylamine), it seems more reasonable to conclude that benzeneazo-β-naphthylamine also contains the NH_2 group. It is impossible to write the formula of this azo-benzylidene compound as a hydrazone, and it is not essential for the explanation of the formation of the triazine that the azo-compound should be formulated on this quinonoïd type. The details of the mode of preparation, and the properties of the triazines which have been investigated, will be given subsequently.

The action of halogens on the azo-derivatives of β-naphthylamine is worthy of further attention, and experiments in this direction have been commenced. Lawson has studied the action of bromine on benzeneazo-β-naphthylamine (*Ber.*, 1886, 18, 2424), but this compound undergoes complete decomposition under the influence of this reagent, the products being dibromo-β-naphthylamine (m. p. 121°)* and brominated phenol. The nitroazo-derivatives of β-naphthylamine appear to be more stable under the influence of halogens.

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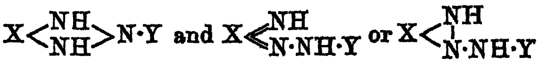
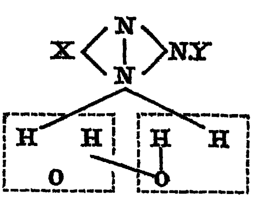
* In 1889 I commenced an investigation of this compound in conjunction with one of my students, Mr. R. E. Evans, who had to abandon the work before its

The experiments recorded in the present communication do not, as we have already stated, furnish any conclusive proof as to the presence or absence of the NH_2 group in these orthoazo-compounds. One of the most forcible arguments that has been adduced in favour of the view that these compounds do not contain this group is the readiness with which they can be oxidised to pseudazimides. It may be urged that it is extremely improbable that NH_2 should lose two atoms of hydrogen on oxidation, as in most, if not all, instances where such loss of hydrogen occurs the two atoms of hydrogen come from *different* atoms of the element with which the hydrogen is combined. The formulæ



$$X{<}{\genfrac{}{}{0pt}{}{NH}{NH}}{>}N{\cdot}Y \text{ and } X{<}{\genfrac{}{}{0pt}{}{NH}{N{\cdot}NH{\cdot}Y}} \text{ or } X{<}{\genfrac{}{}{0pt}{}{NH}{N{\cdot}NH{\cdot}Y}}$$

are thus regarded by many chemists as being more in harmony with the properties of these compounds. It is, however, most probable that the process of oxidation does not consist simply in the removal of two atoms of hydrogen, but that water takes part in the reaction, as in so many other cases of oxidation, such as the formation of acids from aldehydes, of quinones from amines, paradiamines, paramidophenols, &c. It is possible to construct numerous formulæ representing the formation of the pseudazimide by the joint action of oxygen and water, even on the old view of the constitution of the orthamidoazo-compounds. From the view that these compounds contain one atom of quinquevalent nitrogen, the oxidation may be represented by the scheme



completion. As the research was left too incomplete for publication, the results have not been made known. Claus and Philipson have, however, recently gone over the same ground (*J. pr. Chem.* [2], 43, 47), and have arrived at the same results, although we differ slightly in some of our melting points. The dibromonaphthalene (1 : 3′) obtained by us from Lawson's dibromonaphthylamine, m. p. 121° (obtained by brominating benzeneazo-β-naphthylamine in acetic acid solution), by means of the diazo-reaction with absolute alcohol, after purification by steam-distillation and crystallisation from alcohol, formed white (not pale yellow) needles melting at 59° (C. and P. give 61°). The tribromonaphthalene obtained by us, after crystallisation from glacial acetic acid, formed small, white needles melting at

We have, in conclusion, to express our thanks to Messrs. Frederick S. Bayley and Martin O. Forster for the valuable aid which they have rendered during the course of this investigation.

Finsbury Technical College.

XLIII.—*On some New Addition Compounds of "Thiocarbamide" which afford Evidence of its Constitution.*

By J. Emerson Reynolds, M.D., F.R.S., Professor of Chemistry, University of Dublin.

In the course of Part IV of a series of papers on "Silicon Compounds and their Derivatives" (Trans., 1888, **53**, 857), I gave some account of a beautiful, white, crystalline substance which was one of the most abundant products of the action of ethylic alcohol on the compound $(H_4N_2CS)_8SiBr_4$, described in a previous communication (Trans., 1887, **51**, 202). The product referred to was shown to consist of the elements of 4 mols. of thiocarbamide and 1 mol. of ammonium bromide, whilst its synthesis was effected very simply by heating together the two substances in the above proportions and in presence of absolute alcohol.

It was also pointed out that other halogen compounds of ammonium and of some of its derivatives could be made to unite with thiocarbamide, and afford substances similar to tetrathiocarbamidammonium bromide. But the members of this group of compounds —other than the first—were only mentioned incidentally, as they had not been examined in detail at the time of publication of the paper in which the products of the decomposition of the silicon compound were described. When closely studied, however, they proved to be of more interest than I had supposed, for it soon became evident that they do not all conform to a single type, but exhibit significant variations in composition which is connected with the peculiar constitution of thiocarbamide.

In the following account of these compounds, I shall first describe their preparation and properties, then give a summary of these facts, and conclude with some considerations suggested by the evidence.

116° (C. and P. give 118°). The dibromonaphthylamine gave on oxidation with dilute nitric acid the bromophthalic acid (m. p. 168°), that is, $C_6H_4Br(COOH)_2 = 1:3:4$. The products of oxidation of the dibromonaphthalene were not examined by us. The most noteworthy character of this dibromonaphthalene is the readiness with which it passes over in a current of steam.—R. M.

In the descriptive part, I have given some further details relating to the ammonium bromide compound, as an interesting practical application of the substance has recently been made by Colonel Waterhouse to the production of direct *positive* photographs. So effective is this agent in securing the reversal of the photographic image on gelatino-bromide films, that the presence of less than $\frac{1}{100}$th of a grain per ounce in "eikonogen" developer causes the negative image that first appears to change into a rich-coloured positive.

DESCRIPTIVE PART.

A. *Compounds of Thiocarbamide with Ammonium Haloid Salts.*

It has been already mentioned that the well-defined, crystalline solid $(H_4N_2CS)_4NH_4Br$ was obtained, in the first instance, by the action of ethylic alcohol on the compound which results from the union of silicon tetrabromide with 8 mols. of thiocarbamide; and that the same substance was subsequently prepared by the direct action of ammonium bromide on thiocarbamide. The latter or synthetic method is the only one with which I am now concerned; it afforded the best result when conducted in the following manner:--

10 grams of ammonium bromide were dissolved in the smallest quantity of hot alcohol required for its solution, and this liquid was added to a boiling and nearly saturated alcoholic solution containing 30 4 grams (4 mols.) of thiocarbamide. The mixture was boiled for five minutes, and then allowed to cool in the containing flask. The contents soon began to deposit warty aggregations of radiating crystals which attached themselves to the bottom and sides of the vessel, and, when quite cold, the whole formed a nearly solid and beautiful, white, crystalline mass of characteristic appearance. When drained, pressed, and recrystallised from alcohol, it is obtained in a perfectly pure state In this condition it was analysed, with the results already stated (*loc. cit*).

Tetrathiocarbamidammonium bromide melts at 173—174°, but begins to decompose at 178—180°. It is easily soluble in boiling absolute alcohol, but is so much less soluble in the cold liquid, that the hot saturated solution becomes nearly solid at ordinary temperatures. More dilute solutions, when slowly cooled, deposit the compound in large and beautiful stellate groups of crystals which often resemble sea anemones in appearance. It is almost insoluble in ether, chloroform, and benzene, but is rather easily soluble in water. When pure, its aqueous solution can be boiled violently for half an hour without undergoing sensible decomposition; but if impure in the first instance, partial decomposition occurs. It is easily broken up by boiling with dilute acids and alkalis, and is readily desulphurised by alkaline lead tartrate.

Having determined the composition and principal properties of the tetrathiocarbamide compound, it remained to be seen whether ammonium bromide could combine with 1, 2, or 3 mols. of thiocarbamide in presence of alcohol. To test this point, three separate experiments were made, in each of which 1 molecular proportion of ammonium bromide was heated in alcoholic solution with 1, 2, and 3 mols. respectively of thiocarbamide under precisely the same conditions as those which suffice for the production of the tetrathiocarbamide compound. In each case a quantity of the tetrathiocarbamidammonium bromide was obtained proportional to the amide added, and the excess of ammonium bromide separated when the mother liquors were concentrated. No traces were observed of any but the tetra-compound, under the above-mentioned conditions, or under any other hitherto tried.

It therefore appears that ammonium bromide and thiocarbamide do not combine in any other proportion than that of 1 mol. of the former to 4 mols. of the amide.

A compound of ammonium iodide with thiocarbamide was obtained in the same way as the bromide; that is to say, 3·6 grams of ammonium iodide and 7·6 grams of thiocarbamide (1 : 4 mols.) were dissolved in separate quantities of hot alcohol; the solutions were then mixed, and the mixture boiled. Combination took place as in the case of the bromide, and a similar felted mass of crystals separated on cooling. The product was washed with cold alcohol, twice recrystallised from the same solvent, and dried.

The melting point of the pure compound is 186°, but the substance begins to decompose at about 190°.

I. 0·27 gram gave 0·545 $BaSO_4$.
II. 0·2475 gram gave 0·131 AgI.

The formula $(H_4N_2CS)_4NH_4I$ requires :—

	Theory.	Found.
S	28·50 per cent.	28·74 per cent.
I	28·28 „	28·60 „

There is, therefore, no doubt that the compound formed by ammonium iodide is similar in composition, as well as in general characters, to that afforded by ammonium bromide with thiocarbamide.

An ammonium chloride compound with thiocarbamide was prepared as follows :—1 gram of pure ammonium chloride was dissolved in the least possible quantity of boiling 85 per cent. alcohol, and was added to a solution, also boiling, of 6 grams (or rather more than 4 mols.) of thiocarbamide in alcohol. Combination took place, and a felted, crystalline mass separated on cooling, closely resembling the bromide of ammonium compound. The substance was recrystallised from boiling alcohol, washed well with cold spirit, and dried. Its melting point was 154°.

A sensible excess of thiocarbamide was used in this preparation, and the crystalline product seems to have the power of carrying down with it and retaining persistently some of the free amide, and as repeated crystallisation from even moderately strong alcohol tends to decompose it, in the following sulphur and chlorine determinations the former is high and the halogen proportionately low.

I. 0·3535 gram gave 0·9447 $BaSO_4$.
II. 0·256 „ 0·0945 AgCl.

The formula $(H_4N_2CS)_4NH_4Cl$ requires:—

	Theory.	Found.
S	35·80 per cent.	36·74 per cent.
Cl..........	9·93 „	9·12 „

The results indicate that the product obtained is the tetrathiocarbamidammonium chloride analogous to the bromide and iodide. It may be added that only tetrathiocarbamide compounds were produced in the cases of the iodide and chloride, as well as in that of the bromide.

B. *Substituted Thiocarbamides and Ammonium Bromide.*

Experiments were next made with substituted thiocarbamides, in order to ascertain whether they can form compounds with ammonium bromide similar to those obtained with the unsubstituted amide.

The mode of operating was the same as in the cases already described, in which definite compounds were produced, and each of the following mono- and di-substituted thiocarbamides was treated with ammonium bromide.

$CSN_2H_3{\cdot}CH_3$
$CSN_2H_3{\cdot}C_2H_5$
$CSN_2H_3{\cdot}C_3H_5$
$CSN_2H_3{\cdot}C_6H_5$
$CSN_2H_2(C_6H_5)_2$
$CSN_2H_2(C_6H_5){\cdot}COCH_3$.

In no instance was any evidence of combination obtained, even under the most favourable conditions, the unchanged thiocarbamides crystallising out from the solutions along with the ammonium bromide used in these experiments.

Considering the number of substituted thiocarbamides examined, and the variety of radicles present, it is clear that the substitution of even one atom of hydrogen by an alkylic or allied group destroyed the power of the compound to combine with ammonium bromide But it is to be noted that all the thiocarbamides used in the experiments were prepared by similar methods, and were doubtless of similar constitution.

C. *Compounds of Tetrethylammonium Iodide and Bromide with Thiocarbamide.*

The last group of experiments having proved that the introduction of a single alcoholic radicle into thiocarbamide wholly prevented the combination of the product with ammonium bromide, the next step was obviously to ascertain whether the presence of similar radicles in the bromide destroys its power of uniting with unchanged thiocarbamide. Hence a series of experiments were made with the alkylammonium bromides and iodides, the ethylic compounds being those chiefly employed. I shall first describe the results obtained with the tetrethylammonium salts, the iodide being that first used.

Five grams of pure tetrethylammonium iodide were dissolved in alcohol and added to an alcoholic solution of 6 grams (1 : 4 mols.) of thiocarbamide. The mixture was boiled for rather more than an hour. When cold, no crystals were deposited, though the solution was strong; it was therefore distilled down sufficiently and allowed to cool, when a mixed crystallisation was obtained, consisting of free thiocarbamide with fine, prismatic crystals of a compound of the iodide with thiocarbamide, which contained more iodine than is required even for a compound of only 2 mols. of the amide with 1 of the iodide, but no trace of any tetrathiocarbamide compound could be detected, nor was any obtained after further attempts at combination. As the evidence pointed to the production of a dithiocarbamide compound at most, a further calculated quantity of tetrethylammonium iodide was added, so as to secure the proper proportions in solution. On crystallisation after further heating, a fine crop of large, needle-like crystals separated unmixed with free thiocarbamide. But the appearance of the crystals and their manner of separating from solution presented no similarity whatever to the compounds of thiocarbamide with simple ammonium salts. The new substance was recrystallised from alcohol and carefully dried for analysis.

The melting point of the pure compound is 185°.

0·553 gram gave 0·644 $BaSO_4$.

0 3455 .. 0 1974 AgI.

The formula $(H_4N_2CS)_2(C_2H_5)_4NI$ requires:—

	Theory.	Found.
I	31·0 per cent.	30 85 per cent.
S	15·6 „	16 00 „

There is, therefore, no doubt that a well-defined dithiocarbamide compound (and possibly a 1 : 1 also) is formed with tetrethylammonium iodide, but no higher product was obtained, even in presence of a considerable excess of thiocarbamide.

Similar results to the foregoing were afforded by tetrethylammonium bromide; the single compound obtained separated in fine, rectangular prisms, which were sufficiently purified by one crystallisation.

The pure compound melted at 159—160°.

0 2845 gram gave 0·1486 AgBr.
0·3218 „ 0·399 $BaSO_4$.

The formula $(H_4N_2CS)_2(C_2H_5)_4NBr$ requires:—

	Theory.	Found.
Br	22·09 per cent.	22·22 per cent.
S	17·67 „	17·04 „

The solution from which this compound had separated was mixed with excess of thiocarbamide and heated for half an hour to boiling, but no traces of any tetrathiocarbamide compound was obtained in successive crystallisations from the liquid. The chloride seems to act in the same way.

Thiocarbamide, therefore, combines with the haloïd salts of ammonium and tetrethylammonium, but affords two perfectly distinct classes of compounds, differing alike in characters and in composition.

D. *Compounds of Thiocarbamide with partially substituted Alkylammonium Salts.*

The strongly contrasted results afforded by ammonium and by tetrethylammonium salts invested with much interest the examination of any compounds that could be formed by the union of thiocarbamide with partially substituted alkylammonium salts.

The products first obtained by the union of thiocarbamide with primary, secondary, and tertiary ammonium salts appeared to resemble those prepared with the simple ammoniacal haloïd salts as described in A, that is to say, they seemed to be compounds of the tetrathiocarbamidammonium type. But the analytical data obtained with those products were not satisfactory; hence, as soon as time permitted, the work was repeated very carefully, with the results stated below.

The alkylammonium salts used at first were purchased, but those subsequently employed were prepared in my laboratory by the direct action of the required acid on the pure amine, so that ordinary ammoniacal salts were excluded. I shall first describe the results obtained with the diethyl compound; the chief interest attaches to it as being intermediate between ammonium bromide on the one hand and tetralkylic bromide on the other.

A compound of diethylammonium bromide with thiocarbamide was formed when 3·8 grams of the bromide in *absolute* alcohol was boiled with a similar solution of 7·6 grams of thiocarbamide. On cooling, a crop of crystals was obtained which was evidently a mixture of thiocarbamide and a new compound, and contained only 12·08 per cent. of Br, but 31·53 per cent. of S; whilst its melting point was not sharp, liquefaction commenced at 135°, and was not complete under 145°.

The mother liquor, when concentrated, afforded groups of fine, thin prisms, resembling somewhat the ammonium bromide compound in its mode of separation. These crystals were drained, slightly washed with absolute alcohol, and recrystallised from the same solvent.

The melting point of this compound was sharp between 133° and 134°. Some months afterwards this preparation was recrystallised and was found to have the same melting point. It was observed that crystals began to form in the liquid at 174°.

A complete analysis was made with the following results:—

I. 0·3575 gram gave 0·2075 H_2O and 0·2891 CO_2.
II. 0·181 „ 39·3 c.c. of N at 14° and 755 mm.
III. 0·228 „ 0·427 $BaSO_4$.
IV. 0·272 „ 0·131 AgBr.

The formula $(H_4N_2CS)_3H_2(C_2H_5)_2NBr$ requires:—

	Theory.	Found.
C	21·99 per cent.	22·05 per cent.
H	6·28 „	6·44 „
N	25·65 „	25·23 „
S	25·14 „	25·74 „
Br	20·94 „	20·49 „
	100·00	

It is to be noted that this compound is very sensitive to the action of water; anhydrous alcohol must be used in its preparation, and if that used for recrystallisation be much hydrated, a mixed product is obtained which contains free amide and, possibly, a dithiocarbamide compound. Hence great care is required both in the preparation and purification of the trithiocarbamidediethylammonium bromide.

I have not succeeded in preparing a tetrathiocarbamidediethylammonium bromide; if it exists in solution, it is certainly decomposed when crystallisation takes place even from anhydrous alcohol. At the time my former paper was written (*loc. cit.*), only a rapidly crystallised product, from a concentrated solution, had been obtained, and the bromine in that product was found to be near to the percentage required for a tetra-compound, but I am not satisfied that the material then obtained was homogeneous.

Diethylammonium chloride also unites with thiocarbamide and affords a silky mass, which, however, always contains some free thiocarbamide. The best product melted about 136°, but not sharply; and, like the bromide, when heated to 175°, crystals began to form in the molten substance and increased in amount until the whole became nearly solid at 180°.

This somewhat impure material afforded 10·14 per cent. of Cl and 29 90 per cent of S.

A trithiocarbamide compound requires 10·51 per cent. of Cl and 29·95 per cent. of S, while one containing 4 mols. of thiocarbamide requires 8·6 per cent. of Cl and 31 per cent. of S. The latter is, therefore, excluded; hence the crystalline substance examined contains a sensible proportion of free amide adherent to the chloride of trithiocarbamidediethylammonium, analogous to the bromide already described.

Triethylammonium Bromide Compounds with Thiocarbamide.—The earliest small experiment made with the salt and amide seemed to indicate that a tetrathiocarbamide compound was formed, but when the work was repeated on a larger scale, and the product slowly separated from alcoholic solution, it was not found possible to obtain a definite compound with 4 mols. of thiocarbamide under the usual conditions of the series of experiments. In all cases free amine separated along with any substance produced.

The proportion of bromide was then increased so that the solution contained 1 mol. to 3 of thiocarbamide, using 14 grams of the latter, and the materials were heated with absolute alcohol to the boiling point of the latter for three hours. When the liquid was allowed to cool, groups of silky crystals separated, which closely resembled the ammonium bromide compound. These were quickly drained off, washed with cold alcohol, pressed, and dried. The mother liquor, on standing over night, gave some more needles and a small crop of thiocarbamide crystals.

Although microscopic examination of the silky crystals showed that they were all of the same kind, and the ratio of bromine to sulphur in them proved to be 1 : 2·58 or, approximately, 2 : 5, slow recrystallisation failed to give the original substance, but, instead, two distinct forms were obtained—one portion consisting of groups of rather long prisms, resembling nitre in appearance, and the other of somewhat large, modified rhomboids; the latter were in smaller proportion and separated out more slowly, along with some more thiocarbamide.

The nitre-like crystals were separated as far as possible by picking and concentration of the liquids; they were redissolved in as small a quantity of strong alcohol as possible (as a large proportion of hot alcohol seemed to partly decompose the compound), and the crystals were again obtained, but in groups of smaller needles. These, indicated by *A* below, were analysed with the following results:—

0·2490 gram gave 0·4118 gram $BaSO_4$.
0·2222 „ 0·1081 „ AgBr.

When again crystallised from alcohol, a purer specimen of shorter crystals, marked *B*, was obtained: but even when absolute alcohol was used, some thiocarbamide separated from the mother liquor; gradual decomposition was found to follow further attempts at complete purification. The crystals were analysed as under:—

0·25 gram gave 0·4247 $BaSO_4$.
0·2798 „ „ 0·126 AgBr.

The two sets of crystals represent the compound

$$(H_4N_2CS)_3(C_2H_5)_4HNBr$$

in somewhat different states of purity, thus:—

	Theory.	*A* crystals.	*B* crystals.
S	23·41 p. c.	22·7 p. c.	23·28 p. c.
Br	19·51 „	20·7 „	19·16 „

The rhomboidal crystals which separated in small quantity along with the above, when washed with alcohol and recrystallised, were obtained in short prisms, and consist of the compound

$$(H_4N_2CS)_2(C_2H_5)_3HNBr.$$

0·1532 gram gave 0·089 gram AgBr = 24·72 per cent. Br.
Theory for the above compound requires 23·91 per cent. of Br.

The mother liquor ultimately afforded a few fine, large prisms mixed with crystals of the other types, which were richer still in bromine, but the quantity of the material obtained was too small to admit of satisfactory purification for analysis.

Methyl- and Ethyl-ammonium Salts and Thiocarbamide.—The general results of the experiments in this direction were unexpected, as it was found that methylammonium salts combine with thiocarbamide, but those of ethylammonium do *not* under any conditions yet realised. I shall first describe the experiments which led to the definite combination.

3 grams of pure methylammonium bromide were dissolved in the smallest possible quantity of strong alcohol, and added to a boiling alcoholic solution of 7·8 grams of thiocarbamide. Combination took place on continued heating, and the solution when cooled became nearly solid, owing to the separation of a felted crystalline mass very similar in appearance to that afforded by ammonium bromide and the amide under similar conditions. This product was pressed, washed, and recrystallised, and when so purified was found to melt sharply at 138°, or 35° lower than the melting point of the ammonium bromide compound (173—174°).

On analysis, it afforded the following results :—

0·427 gram gave 0·1915 AgBr.
0·3897 „ „ 0·8642 $BaSO_4$.

The compound is therefore $(H_4N_2CS)_4(CH_3)H_3NBr$, which requires

	Theory.	Found.
S	30·76 per cent.	30·48 per cent.
Br	19·23 „	19·08 „

Methylammonium chloride gave a similar compound with thiocarbamide, but it was not examined in detail.

Experiments with ethylammonium salts led to negative results so far as direct union with thiocarbamide is concerned. Ethylamine from various sources was used in the preparation of the salts, and the conditions were varied to a much greater extent than in the previous experiments, but without effect.

As long continued heating to the boiling point of absolute alcohol under atmospheric pressure did not determine combination, 2·5 grams of the pure bromide and 6 grams of thiocarbamide were sealed up in a tube with sufficient alcohol to dissolve the whole at 70°. The tube and its contents were then heated at 110° for two hours, but on cooling no evidence of combination was obtained. The heating was repeated for three hours, but the temperature was maintained at about 135°. On cooling, the contents of the tube now became nearly solid, and the mass resembled the ammonium bromide compound in appearance. When the solid contents were twice recrystallised from alcohol, the product was found to contain bromine and sulphur, and it melted at 175—176°, or very slightly higher than the ammonium bromide compound which it so closely resembled in appearance, and on analysis it proved to be that body.

0 2056 gram gave 0 098 AgBr.
0 2732 „ „ 0·1285 H_2O and 0·1245 CO_2.

	Theory for NH_4Br compound.	Theory for $NEtH_3Br$ compound.	Found.
Br	19 98 p. c.	18·60 p. c.	20·28 p. c.
C	11·99 „	16·76 „	12·42 „
H	4·96 „	5·58 „	5·22 „

The determination of carbon was made because of the wide difference in percentages of that element.

There is no doubt, then, that ethylammonium bromide and 4 mols of thiocarbamide do not directly unite when heated with alcohol at 135°, but rather afford the ammonium bromide compound, with ethyl oxide as a necessary bye-product, according to the equation

$$4H_4N_2CS + N(C_2H_5)H_3Br + C_2H_5{\cdot}OH = (H_4N_2CS)_4NH_4Br + (C_2H_5)_2O.$$

SUMMARY OF THE FACTS.

It has been shown that—

1. Thiocarbamide combines with ammonium bromide, iodide. and chloride at the temperature of boiling alcohol, and forms characteristic compounds of the type $(H_4N_2CS)_4H_4NR'$. But no compounds could be formed under the conditions specified which contained *less* than four molecular proportions of the amide to one of the ammonium haloid salt.

2. The following mono- and di-substituted thiocarbamides failed to afford any compounds with ammonium bromide at the temperature of boiling alcohol, viz.: methyl-, ethyl-, allyl-, phenyl-, diphenyl-, and acetylphenyl-thiocarbamides.

3. Thiocarbamide combines with tetrethylammonium bromide and iodide, and forms well-defined crystalline compounds of the type $(H_4N_2CS)_2Et_4NR'$. But no well-defined substance could be isolated under any of the experimental conditions containing more than 2 mols. of the amide and 1 mol. of the tetrethylammonium salt.

4. Thiocarbamide combines with diethylammonium bromide, and the well-crystallised compound $(H_4N_2CS)_3Et_2H_2NBr$ was separated. If a tetra-compound be formed in solution, it is certainly broken up on slow crystallisation.

5. Thiocarbamide also unites with triethylammonium bromide, and in presence of excess of amide a somewhat felted mass is obtained, which on recrystallisation affords two distinct crystals, namely, $(H_5N_2CS)_3Et_3HNBr$ and $(H_4N_2CS)_2Et_3HNBr$.

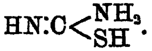
6. With methylammonium bromide, thiocarbamide afforded the compound $(H_4N_2CS)_4MeH_3NBr$, which resembles the corresponding ammonium bromide compound in appearance, but melts at a temperature 34° lower. On the other hand, with *ethyl*ammonium bromide no combination whatever could be effected, and when 4 · 1 mols. of the amide and salt were heated in a pressure tube with alcohol at 135°, ethyl oxide and *tetrathiocarbamidammonium bromide* were the products.

Bearing of the Results on the Question of the Constitution of Thiocarbamide.

Unless thiocarbamide is held to be a tautomeric substance, its constitution may be represented by either of the following formulæ, viz.:—

α-Symmetrical ....

$$CS{<}^{NH_2}_{NH_2}.$$

β-Unsymmetrical .... 

$$HN{:}C{<}^{NH_2}_{SH}.$$

Of late the evidence in favour of the latter constitution has been considerably strengthened, more especially by the careful work of Mr. Emil A. Werner carried on in my laboratory (see Trans., 1890, **57**, 283). I shall now proceed to show that the facts recorded in the present paper supply evidence of a new kind, and altogether in favour of the β- or unsymmetrical structure—at least under the conditions of my experiments.

The readiness with which ammonium bromide, iodide, and chloride form tolerably stable *tetra*thiocarbamide compounds—and only these—is evidently connected with the number of atoms of hydrogen in the ammonium haloid, that is, with the valency of its nitrogen. This necessarily involves the idea of something in the nature of substitution. Moreover, the tendency to form complete and comparatively simple compounds of the order in question must be strong, since we have seen that ethyl is displaced by hydrogen when ethylammonium bromide and 4 mols. of thiocarbamide are heated to 135°, the stable ammonium bromide compound being then formed.

The fact that *none* of the mono- or di-substituted thiocarbamides combine with ammonium bromide under the usual conditions goes far to prove that neither the carbon nor sulphur of thiocarbamide are concerned in the linkage with the ammonium haloïd. It is admitted that alkylic or other radicles of substituted thiocarbamides of the types used are directly united with nitrogen; there is, therefore, no reason why the carbon or sulphur of the primary should be materially affected by such substitution. And further, in regard to sulphur, neither the di- nor tri-ethylammonium bromide compounds formed with thiocarbamide afforded mercaptan or alkylic sulphide or their products when heated to 100° with alkalis and alkaline lead solution, in these particulars differing materially from the action of addition compounds of thiocarbamides of the sulphine class.

On the other hand, the loss of power of combination with ammonium bromide when but one atom of hydrogen in thiocarbamide is displaced by a more positive radicle, such as ethyl or phenyl, is inconsistent with the symmetrical constitution of thiocarbamide, which should still have an NH_2 group unaffected and available for union; but is quite consistent with its unsymmetrical structure.* In the latter case, the two nitrogen atoms are differently engaged, and the genesis of a monosubstituted thiocarbamide from $R{\cdot}N{:}CS$ and ammonia points to the structure $R{\cdot}N{:}C{<}\substack{NH_2\\ SH}$ rather than $HN{:}C{<}\substack{NHR\\ SH}$ for the product. Now the fact that combination takes place with facility between thiocarbamide and ammonium bromide, but not at all with ethyl- or phenyl-thiocarbamide, accords with the structure $RN{:}C{<}\substack{NH_2\\ SH}$, where the presence of the positive radicle in the imidic group paralyses the power of combination, which appears in consequence to be exclusively due to the NH of the substance we have been accustomed to term thiocarbamide. The ammonium bromide compound would therefore become $[NH_2(SH)CNH_2]_4NBr$; but whether union is effected by breaking the double linkage of carbon and NH, or the change of valency of the latter, remains for determination.

In the ammonium bromide compound, the attraction of the components seems to be at a maximum; but whilst substitution in thiocarbamide reduces it to zero, similar substitution in ammonium bromide (save in the case of the ethylammonium salt†) only lessens the power of forming tetra-compounds without destroying it. These facts seem to point to the development of quinquavalence in one of the nitrogen atoms of thiocarbamide in the course of combination.

I think the true "thiocarbamide" is yet to be discovered, and that we must revert to the name "sulphurea" or "thiourea" as the correct designation of the primary substance from which the above compounds have been obtained.

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* From a somewhat similar point of view, the production of a tetra- rather than a di-thiocarbamide compound is inconsistent with the symmetrical structure.

† Whose non-combination may be more apparent than real if formed and decomposed at nearly the same temperature level.

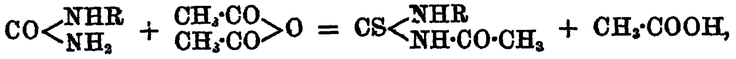
XLIV.—*Action of Acetic Anhydride on Substituted Thiocarbamides, and on an Improved Method for Preparing Aromatic Thiocarbimides.*

By Emil A. Werner, Assistant Lecturer in Chemistry, Trinity College, University of Dublin.

During the progress of an investigation, part of which has already appeared in this Journal (Trans., 1890, 283), on the "Action of the Alkylogens on certain Substituted Thiocarbamides," an experiment was made, in the hope of obtaining an acetylated diphenylthiocarbamide, of the composition $\mathrm{CS}\!<\!\begin{matrix}\mathrm{N{\cdot}COCH_3{\cdot}C_6H_5}\\\mathrm{NH{\cdot}C_6H_5}\end{matrix}$, for the subject of further study.

This experiment, described below, was the origin of the investigation detailed in the following pages.

Since the action of acetic anhydride on mono-substituted thiocarbamides is well known to take place in accordance with the equation



$$\mathrm{CO}\!<\!\begin{matrix}\mathrm{NHR}\\\mathrm{NH_2}\end{matrix} + \begin{matrix}\mathrm{CH_3{\cdot}CO}\\\mathrm{CH_3{\cdot}CO}\end{matrix}\!>\!\mathrm{O} = \mathrm{CS}\!<\!\begin{matrix}\mathrm{NHR}\\\mathrm{NH{\cdot}CO{\cdot}CH_3}\end{matrix} + \mathrm{CH_3{\cdot}COOH},$$

a similar reaction, using diphenylthiocarbamide, seemed the most promising method for obtaining the desired derivative. Hence, with this object in view, the primary experiment was carried out as follows:—

Action of Acetic Anhydride on Symmetrical Diphenylthiocarbamide.

Exp. 1. In a flask, furnished with a reflux condenser, 10 grams of the urea and 10 grams of acetic anhydride were mixed, and the mixture heated to boiling for two hours. The quantity of the anhydride used represents a slight excess over 2 molecular proportions, and, whilst it is scarcely sufficient to even moisten the urea in the cold, the latter enters completely into solution before the boiling point (138°) of the anhydride is reached.

The product, which had assumed a dark, reddish-brown colour during the ebullition, smelt distinctly of phenylthiocarbimide; it was, therefore, while still warm, mixed with about five times its weight of hot water, and immediately subjected to distillation in a current of steam. After half an hour's distillation, no perceptible amount of the thiocarbimide was obtained, the quantity being merely sufficient to impart its characteristic odour to the aqueous distillate. The residue in the distillation flask was completely dissolved in a sufficient amount of boiling water, and the hot solution quickly filtered from a trace of dark-brown, tarry matter. On cooling, a considerable quantity of beautiful, flat, glistening prisms separated; these, after being collected and dried, were found to possess all the appearance and properties of acetanilide.

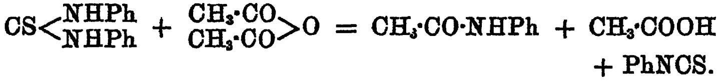
The crystals melt at 112—113°; m. p. of acetanilide, 112°. A combustion of a specimen purified by recrystallisation from benzene placed the identity of the substance beyond doubt.

0·2440 gram gave 22·6 c.c. nitrogen at 10° and 749·5 mm.
0·2442 „ 0·154 gram H_2O, 0·636 gram CO_2.

	Found.	Theory for acetanilide.
C	71·02 per cent.	71·11 per cent.
H	7·00 „	6·66 „
N	10·87 „	10·37 „

From the original mother liquor, two crops of crystals and a final residue were obtained; in each case, after purification, the substance melted at 112—114°, and possessed the properties of acetanilide.

Therefore the principal product of the action of acetic anhydride on sulphocarbanilide, under the above conditions, is simply acetanilide, the sulphur of the urea being expelled in a gaseous form. The fact that phenylthiocarbimide was recognised in the product suggested at once that the acetanilide of the foregoing experiment was the result of *at least* two distinct actions, namely:—

(1.) 

$$CS\left<\begin{matrix}NHPh\\NHPh\end{matrix}\right. + \left.\begin{matrix}CH_3\cdot CO\\CH_3\cdot CO\end{matrix}\right>O = CH_3\cdot CO\cdot NHPh + CH_3\cdot COOH + PhNCS.$$

(2.) $CH_3\cdot COOH + PhNCS = CH_3\cdot CO\cdot NHPh + COS.$[*]

Whether the first equation is preceded by the formation of the desired acetylated derivative of the urea, is a question which has been decisively answered in the negative by the results of the experiments recorded in the present paper.

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[*] This equation calls for a few remarks, before proceeding further. The interaction of glacial acetic acid and phenylthiocarbimide has already been the subject of single, but by no means exhaustive, experiments by Hofmann (*Ber.*, 3, 770), and later on by Claus and Voëltzkow (*Ber.*, 14, 445). According to the former, the products are *diacetanilide*, CO_2, and H_2S, whilst the latter state that acetanilide, H_2S, COS, and CO_2 are the products. In connection with the present work, I have made a careful re-investigation of the subject (the results will shortly be given in a separate paper), and find that *pure* acetic acid and phenylthiocarbimide interact in strict accordance with the above equation. Moreover, I find that the substance hitherto described as diacetanilide is simply acetanilide, the former being unknown up to the present time, and while I have made several different experiments in the hope of isolating that compound, I believe that I have been so far unsuccessful, and I may add that my results in this direction are quite in agreement with those recently published by Dr. J. B. Cohen (Trans., 1891, 59, 67) concerning the isolation of dibenzanilide; indeed unexpected difficulties appear to surround the preparation of the "dianilides."

The total weight of acetanilide obtained was 9·8 grams, theory being 11·84 grams. The deficiency is explained—

1st. By the fact that some of the thiocarbimide escaped decomposition, and some probably volatilised with the COS gas.

2nd. I find that acetanilide is, to a slight extent, volatilised undecomposed in a current of steam.

And while, so far as it affects the results of the present investigation, it may be assumed that acetanilide was the sole crystalline product of the reaction, on the other hand, I have little doubt that a very small quantity of a second body accompanies the acetanilide, resulting (as I have ascertained by direct experiments) from a slight secondary reaction between acetic anhydride and the phenylthiocarbimide; this body, which bears a great resemblance to acetanilide, I have not yet identified; it may suffice, for the present, to say that it is not diacetanilide, as might have been expected, but a substance *richer in nitrogen* than acetanilide itself, and raising the melting point of the latter by its presence.

Exp. 2. An experiment was now conducted with a view of ascertaining how far this rather remarkable decomposition of sulphocarbanilide by acetic anhydride is under control; in other words, does the second stage of the decomposition commence only on the completion of the first, or does it immediately succeed the initial phase in this decomposition, and are the two reactions, therefore, for all practical purposes, proceeding simultaneously?

The same quantities of material were used as before, the ebullition was continued until the gas evolved at the top of the vertical condenser produced a slight blackening on a piece of bibulous paper moistened with an alkaline lead solution, or ammonio-nitrate of silver, tests for COS. This occurred at the end of *seven and a half minutes* boiling, and marked the commencement of the second stage in the decomposition. The product was immediately treated with hot water, and subjected to steam-distillation. Phenylthiocarbimide in quantity quickly passed over into the receiver, and, after 40—50 minutes distillation, its separation from the residue was practically complete. It was easily collected by subsidence, and, after removal by means of a separating funnel and subsequent exposure for a short time over oil of vitriol, it was weighed with the following result:—

Theoretical yield of PhNCS = 5·92 grams.
Weight obtained = 5·40 grams = 91·21 per cent. of theoretical.

The weight of acetanilide obtained from the residue in the distillation flask was 6·03 grams, that is, a slight excess over the theoretical (5·92 grams) calculated on the *first equation only.* This proved that the latter had been slightly overstepped, even in the above experiment, and that by a small reduction in the period of ebullition a still sharper result was to be hoped for.

Exp. 3. Ten grams each of sulphocarbanilide and acetic anhydride. Period of ebullition, *five minutes.*

Product treated with water, and immediately steam-distilled.

Phenylthiocarbimide obtained = 5·72 grams or 96·62 per cent. of theoretical.

Acetanilide, crude, obtained = 5·78 grams or 97 62 per cent. of theoretical.

To attempt any great accuracy in the estimation of either product was considered superfluous; bearing in mind the modest aim of the experiment, and considering the rather small scale on which the experiment was conducted, I think the above results prove conclusively that the two stages in the decomposition of thiocarbanilide by acetic anhydride are sharply marked.

The first stage is fully realised *after five minutes ebullition at* 138°, before the second stage has time to enter on its course. While we have, therefore, in the above reaction a much more rapid and productive method of preparing phenylthiocarbimide than has been hitherto known, the yield of it is, on the other hand, remarkably sensitive to the influence of time under the above conditions of temperature, and unless the conditions under Exp. 3 be strictly observed, an almost theoretical yield of the thiocarbimide will not be obtained.

The rate at which the second equation proceeds, when once started, is shown in the results of the following series of experiments (in which I have included Exps. 2 and 3).

The yield of phenylthiocarbimide alone is given, and I may just add that the deficiency of the thiocarbimide *below* five minutes is due to incomplete decomposition of the thiocarbanilide, whilst in all other cases it is due to the second stage of the decomposition, the proportion of acetanilide increasing in proportion to the diminution in the yield of thiocarbimide.

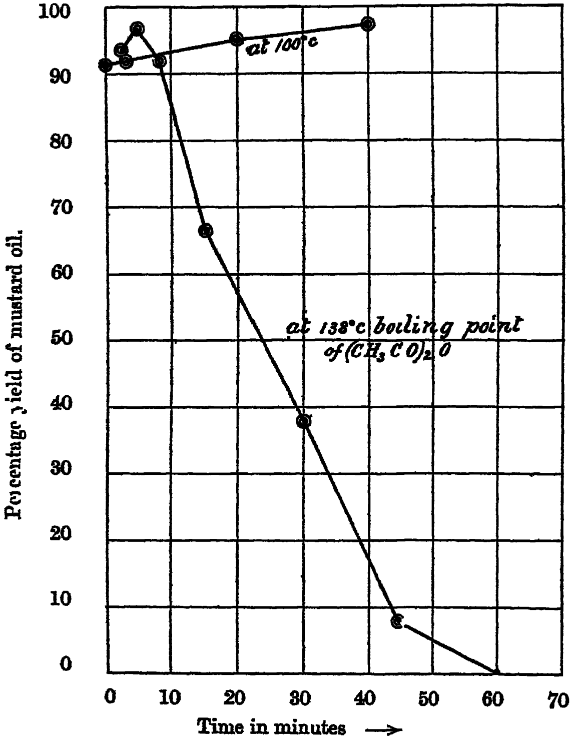
Yields of Phenylthiocarbimide from Sulphocarbanilide at the Boiling Point of Acetic Anhydride.

10 grams of the urea used. Theoretical yield of the thiocarbimide 5·92 grams.

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 4.	2½ minutes.	5·47 grams.	92·39 per cent.
„ 3.	5 „	5·72 „	96 62 „
„ 2.	7½ „	5·40 „	91·21 „
„ 5.	15 „	3·90 „	65·87 „
„ 6.	30 „	2·20 „	37·16 „
„ 7.	45 „	0·42 „	7·09 „
„ 8.	60 „	0·00 „	0·00 „

A graphic representation of the rate of fall in the yield of the thiocarbimide is shown in the curve in Fig. 1, plotted from these results.

FIG. 1.—Curves illustrating influence of time on the yield of phenyl mustard oil from sulphocarbanilide at 100° and 138° C. respectively.



The decomposition of sulphocarbanilide by the anhydride, at the temperature of the water-bath, was next studied.

The following are the details of the first experiment carried out under these conditions, in the last hope of obtaining an acetylated derivative.

Exp. 9.—10 grams of the urea and 10 grams of the anhydride were slowly heated on the water-bath; dissolution of the urea commenced at 75°, and was just complete when the temperature had reached 97°. Eight minutes were required for the heating from 75° to 97°. The product was at once removed from the source of heat, water added, and mixture subjected to steam-distillation.

Phenylthiocarbimide obtained, 5·4 grams = 91·21 per cent.
Acetanilide „ 5·42 „ = 91·55 „

while 0·42 gram of unchanged thiocarbanilide was obtained as a residue insoluble in boiling water.

This almost theoretic decomposition of thiocarbanilide under such "mild" conditions is without parallel in any of the reactions hitherto studied for the production of the thiocarbimide.

The remaining experiments show that the yield of the thiocarbimide is not materially affected by prolonged heating on the water-bath.

Yield of Phenylthiocarbimide at 100°.

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 10.	3 minutes.	5·42 grams.	91·55 per cent.
„ 11.	20 „	5·58 „	94·25 „
„ 12.	40 „	5·72 „	96·62 „

Hence, as regards the yield of thiocarbimide, the same result is obtained, either by heating at 138° for five minutes, or at 100° for 40 minutes.

From the results of the second series of experiments the two following conclusions are arrived at:—

1. The mere act of dissolving thiocarbanilide in acetic anhydride is accompanied by simultaneous decomposition into thiocarbimide and acetanilide, and there is therefore no acetylated urea formed.

2. At 100°, the decomposition is restricted to a single stage, and the yield of thiocarbimide is not diminished by increasing the time of heating.

In order to establish, if possible, the generic character of the decomposition just investigated, the action of acetic anhydride on the three symmetrical ditolylthiocarbamides, and on metadixylylthiocarbamide, was next studied.

The experiments were carried out in exactly the same manner as those already described; I have contented myself by giving the yields of the thiocarbimide alone in each case, and I may just add that the variations in the yield of "acetotoluides" and "acetoxylide" follow the same order as in the case of the acetanilide.

Acetic Anhydride and Diorthotolylthiocarbamide.

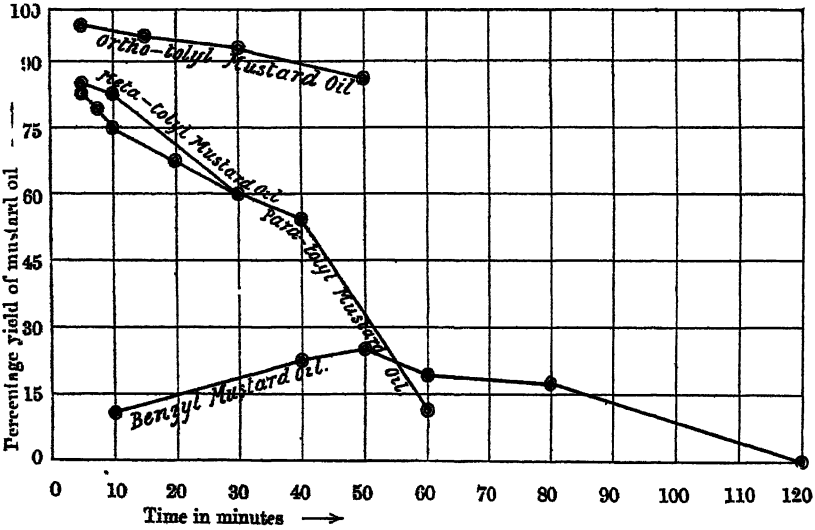
The symmetrical thiocarbamide used in the following experiments was prepared from orthotoluidine and carbon bisulphide. In each case. 12·8 grams of the thiocarbamide were heated with 10·2 grams of acetic anhydride, this being in the proportion of 1 mol. of the urea and 2 mols. of the anhydride.

Yields of Orthotolylthiocarbimide from $CS(NH{\cdot}C_7H_7)_2$ *at the Boiling Point of Acetic Anhydride.*

Theoretical yield of $C_6H_4(CH_3){\cdot}NCS$ [1 : 2] 7·45 grams.

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 13.	5 minutes.	7·22 grams.	96·91 per cent.
„ 14.	15 „	7·10 „	95·30 „
„ 15.	30 „	7·05 „	94·63 „
„ 16.	50 „	6·55 „	87·91 „

Fig. 2.—Curves illustrating the influence of time on the yield of mustard oils from the three isomeric ditolylthiocarbamides, and from the isomeric dibenzylthiocarbamide, at the boiling point of acetic anhydride.



Hence, while *five minutes* ebullition, the same conditions as in the case of thiocarbanilide, give the best yield of thiocarbimide, the rate at which the latter disappears from secondary decomposition is extremely slow.

A graphic representation of this is given in the curve, Fig. 2 (p. 402).

Acetic Anhydride and Dimetatolylthiocarbamide.

The symmetrical thiocarbamide used in these experiments was prepared from metatoluidine and carbon bisulphide.

The quantity of material at my disposal was very limited in this case; hence the experiments were carried out on a smaller scale than was otherwise desirable.

The quantities used were 8 grams of dimetatolylthiocarbamide and 6 4 grams of acetic anhydride, the molecular ratios being the same as before.

Yields of Metatolylthiocarbimide from $CS(NH{\cdot}C_7H_7[m])_2$ *at the Boiling Point of Acetic Anhydride.*

Theoretical yield of $C_6H_4(CH_3){\cdot}NCS$ [1 : 3] 4·65 grams.

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 17.	5 minutes.	4·07 grams.	87·52 per cent.
„ 18.	10 „	3·82 „	82·15 „
„ 19.	30 „	2·80 „	60·21 „

Here again, *five minutes* ebullition afforded the best yield of the thiocarbimide, and whilst the latter is not so high as might have been expected, this I attribute in great measure to the small scale of the experiments, the unavoidable loss in the collection of the thiocarbimide introducing an unfavourable source of error which is magnified on account of the small quantities of the thiocarbimide actually yielded.

In this case it is seen that, while the rate of fall in the yield of thiocarbimide is much more rapid than in the case of the isomeric orthotolylthiocarbamide, it proceeds at only about half the rate as compared with sulphocarbanilide.

Acetic Anhydride and Diparatolylthiocarbamide.

The thiocarbamide used was prepared from paratoluidine and carbon bisulphide.

In this case the quantities used were the same as in the case of the orthotolyl isomer,

Namely, 12 8 grams diparatolylthiocarbamide and 10·2 grams acetic anhydride.

Yields of Paratolylthiocarbimide from $CS(NH·C_7H_7[p])_2$ *at the Boiling Point of Acetic Anhydride.*

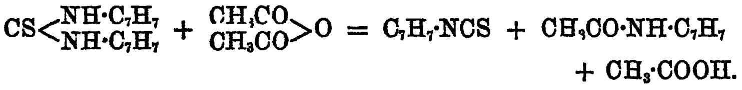
Theoretical yield of $C_6H_4(CH_3)·NCS$ [1:4] 7 45 grams.

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 20.	5 minutes.	6·37 grams.	85·50 per cent.
„ 21.	7½ „	5·85 „	78·52 „
„ 22.	10 „	5·57 „	74·76 „
„ 23.	20 „	5·02 „	67 38 „
„ 24.	40 „	4 15 „	55·70 „
„ 25.	60 „	0·85 „	11·40 „

Whilst here again the best yield of thiocarbimide has been after *five minutes* ebullition, yet it is not quite so high as might have been expected; this is due in the case of the diparatolylthiocarbamide to the fact that the second stage of the decomposition commences its course before the first stage has been fully completed.

In support of this statement, I shall give the weights of paracetotoluide (m. p. 146·5°) recovered from Exps. 20 and 21 respectively.

Calculated on the first decomposition only, viz.:—



$$CS\!\left\langle\begin{array}{l}NH·C_7H_7\\NH·C_7H_7\end{array}\right. + \left.\begin{array}{l}CH_3CO\\CH_3CO\end{array}\right\rangle O = C_7H_7·NCS + CH_3CO·NH·C_7H_7 + CH_3·COOH.$$

The theoretical yield of paracetotoluide is 7·45 grams.

Exp. 20. Paracetotoluide obtained 7·2 grams.
Exp. 21. „ „ 8·15 „

In addition, 0 51 gram of unchanged diparatolylthiocarbamide was recovered from Exp. 20, a proof that the first stage of the decomposition was not yet complete; on the other hand, the slight excess in the yield of paracetotoluide after an increase of only two and a half minutes ebullition, proves that the second stage of the reaction had already commenced.

Acetic Anhydride and Metadixylylthiocarbamide.

The thiocarbamide was prepared from commercial pure metaxylidine boiling at 212° and carbon bisulphide. The quantities used in each experiment were 12 grams of the urea and 8·7 grams of the anhydride.

Yields of Metaxylylthiocarbimide from $CS(NH{\cdot}C_8H_9)_2$ *at the Boiling Point of Acetic Anhydride.*

Theoretical yield of $C_6H_3(CH_3)_2{\cdot}NCS$ [1 : 3 : 4] 6·88 grams.

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 26.	5 minutes.	6·05 grams.	87 93 per cent.
„ 27.	10 „	6·00 „	87·20 „
„ 28.	20 „	5·52 „	80 23 „
„ 29.	40 „	4·80 „	69·76 „
„ 30.	60 „	4·40 „	63·95 „

Five minutes ebullition in this case also has afforded the best yield of the thiocarbimide, but for the same reasons as in the case of the paratolylthiocarbimide. I have not been able to obtain a higher yield. The rate at which the second reaction proceeds is nearly as slow as with orthoditolylthiocarbamide.

The results are shown in the form of a curve, in Fig. 2 (p 402).

Metaxylylthiocarbimide forms crystals which melt at 31·5°; it possesses very little odour.

As proof that no acetylated thiocarbamide is formed from the four ureas just studied, I give the results of experiments carried out at the temperature of the water-bath.

The quantities used were the same as before, the mixture was heated on the boiling water-bath until the last portions of the urea had just dissolved, and the product immediately steam-distilled.

The degrees of solubility being different, the actual time of heating varies in each case.

Yield of Thiocarbimides at 100°.

*Ortho*tolylthiocarbamide—

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 31.	10 minutes.	5 95 grams.	79·86 per cent.

*Meta*tolylthiocarbamide—

	Time.		
Exp. 32.	8 minutes.	4·00 grams.	86·02 per cent.

*Para*tolylthiocarbamide—

	Time.		
Exp. 33.	20 minutes.	6·15 grams.	82·54 per cent.

*Meta*xylylthiocarbamide—

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 34.	30 minutes.	6·00 grams.	87·20 per cent.

In each case, a small amount of the *unaltered* thiocarbamide was recovered.

Having established the reaction, as general, for the aromatic thiocarbamides, the question whether the fatty derivatives are susceptible of a similar sharp decomposition was next studied.

Acetic Anhydride and Dibenzylthiocarbamide.

A quantity of symmetrical dibenzylthiocarbamide was prepared by heating the thiocarbamate, resulting from the interaction of benzylamine and carbon bisulphide, until hydrogen sulphide ceased to be evolved.

Pure dibenzylthiocarbamide melts at 146°, and not at 114°, as stated by Strakosch. The melting point was verified with a specimen prepared directly from benzylthiocarbimide and benzylamine.

I shall give the details of the first experiment in full, as the general results differ considerably from those hitherto obtained.

Exp. 35. Quantities employed, 12·8 grams dibenzylthiocarbamide and 10·2 grams acetic anhydride.

The proportion of anhydride is just sufficient to completely dissolve the urea before the commencement of the ebullition.

The mixture was heated to boiling for *ten minutes*, water added, and immediately subjected to steam-distillation.

Weight of benzylthiocarbimide obtained = 0·9 gram = 12·08 per cent. of theoretical.

In this, and succeeding experiments, it was found best to estimate the quantity of the thiocarbimide by conversion into monobenzylthiocarbamide by means of alcoholic ammonia.

From the residue in the distillation flask, boiling water extracted only 0·98 gram of a substance, which, after purification, melted at 57—58°, and possessed the properties of benzylacetamide, $CH_3{\cdot}CONH{\cdot}CH_2Ph$; m. p. 57°.

The final residue, forming the main bulk of the product, was dissolved in the minimum quantity of boiling alcohol; from the solution, small, well-defined, rhombic prisms quickly separated on cooling.

After three crystallisations from alcohol, a specimen of the new substance was obtained for analysis, in perfectly colourless crystals melting at 93°.

The following data prove the substance to be the expected *acetyldibenzylthiocarbamide*, $CS(NH{\cdot}CH_2{\cdot}C_6H_5)(N{\cdot}CO{\cdot}CH_3{\cdot}CH_2{\cdot}C_6H_5)$:—

I. 0·2385 gram gave by Carius' method, followed by fusion with KNO_3, 0·1895 gram $BaSO_4$.

II. 0·2307 gram gave 20·5 c.c. nitrogen at 12° and 714·5 mm.

	Found.	Theory for acetyl-dibenzylthiocarbamide.
S........	10·91 per cent.	11·34 per cent.
N........	10·26 „	9·91 „

The total weight of crude product obtained was 12·2 grams.

Acetyldibenzylthiocarbamide is readily soluble in alcohol, ether, chloroform, and benzene, moderately in carbon bisulphide and practically insoluble in water.

The alcoholic solution is not desulphurised by boiling with alkaline lead solutions; with ammoniacal silver nitrate, it gives a white precipitate in the cold; this is only slowly blackened on boiling.

Under normal pressure, the urea partly decomposes on distillation, yielding between 175 and 180°, a dark-red oil, comparatively rich in sulphur, whilst between 180 and 190°, the distillate solidifies to a crystalline substance, which, after purification, forms colourless crystals melting at 60—61°, and free from sulphur. The nature of the decomposition has not yet been investigated, but the chief point of interest for the present lies in the fact that not even the odour of benzylthiocarbimide was recognised during the whole time of distilling the thiocarbamide.

Whilst the results of the foregoing experiment show that an acetylated derivative is the first product of the action of acetic anhydride on dibenzylthiocarbamide,* yet the facts show that the derivative in question is susceptible of a secondary decomposition under the conditions of the experiment, whereby some thiocarbimide is generated.

Direct experiment has shown that when acetyldibenzylthiocarbamide is heated to boiling with either glacial acetic acid or acetic anhydride, it is decomposed slowly into the thiocarbimide and benzylacetamide.

Attempts to obtain a high yield of thiocarbimide have proved unsuccessful, the third stage in the decomposition (corresponding to the second stage of the aromatic thiocarbamides) proceeding almost simultaneously with the generation of the mustard oil.

The following are the results:—

Yields of Benzylthiocarbimide from Dibenzylthiocarbamide at the Boiling Point of Acetic Anhydride.

Theoretical yield of $C_6H_5{\cdot}CH_2{\cdot}NCS$, 7·45 grams.

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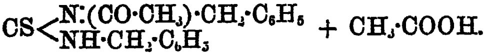
* Though dibenzylthiocarbamide contains the phenyl group, yet its general behaviour is that of a purely fatty thiocarbamide.

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 35.	10 minutes.	0·9 gram.	12·08 per cent.
,, 36.	40 ,,	1·66 ,,	22·33 ,,
,, 37.	50 ,,	1·88 ,,	25·23 ,,
,, 38.	60 ,,	1·43 ,,	19·19 ,,
,, 39.	80 ,,	1·34 ,,	18·04 ,,
,, 40.	120 ,,	0·00 ,,	00·00 ,,

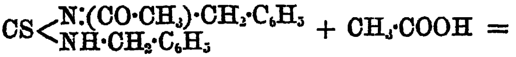
In Exp. 40, where the heating was prolonged for two hours, the final product was simply pure benzylacetamide, $CH_3{\cdot}CO{\cdot}NH{\cdot}CH_2Ph$, the result of three distinct reactions, viz.:—

(1.) $CS(NH{\cdot}CH_2{\cdot}C_6H_5)_2 + (CH_3{\cdot}CO)_2O =$



$$CS\langle\begin{array}{l}N{:}(CO{\cdot}CH_3){\cdot}CH_2{\cdot}C_6H_5\\NH{\cdot}CH_2{\cdot}C_6H_5\end{array} + CH_3{\cdot}COOH.$$

(2.)



$$CS\langle\begin{array}{l}N{:}(CO{\cdot}CH_3){\cdot}CH_2{\cdot}C_6H_5\\NH{\cdot}CH_2{\cdot}C_6H_5\end{array} + CH_3{\cdot}COOH =$$

$$C_6H_5{\cdot}CH_2{\cdot}NCS + C_6H_5{\cdot}CH_2{\cdot}NH_2 + (CH_3{\cdot}CO)_2O.$$

(3.) $C_6H_5{\cdot}CH_2{\cdot}NCS + CH_3{\cdot}COOH = CH_3{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5 + COS.$

A curve showing the comparison of the yield of the thiocarbimide with the three isomeric ditolylthiocarbamides is given in Fig. 2 (p. 402).

Acetylmonobenzylthiocarbamide, $CS\langle\begin{array}{l}NH{\cdot}CH_2{\cdot}C_6H_5\\NH{\cdot}CO{\cdot}CH_3\end{array}$.

This compound was incidentally prepared by boiling monobenzylthiocarbamide with 2 molecular proportions of acetic anhydride for half an hour with reflux condenser. It crystallises readily from alcohol in small, colourless, thin, shining prisms melting at 129—130°.

Analytical data :—

0·282 gram gave 0·3174 gram $BaSO_4$.

	Found.	Theory for $CS(NH{\cdot}CH_2Ph)(NH{\cdot}COCH_3)$.
S	15·47 per cent.	15·38 per cent.

Acetylbenzylthiocarbamide is readily soluble in hot alcohol, rather sparingly in the cold, easily soluble in chloroform, ether, and in warm benzene, practically insoluble in water.

Unlike the corresponding dibenzyl derivative, its alcoholic solution is easily desulphurised on boiling it with alkaline lead solution, and with ammoniacal silver nitrate it gives a white precipitate in the cold, which darkens on standing, and is immediately blackened on boiling.

On distillation, it decomposes, yielding $CH_3{\cdot}CO{\cdot}NCS$ and benzylamine, and also benzylthiocarbimide and acetamide.

Acetic Anhydride and Diethylthiocarbamide.

In this case, the results, though somewhat better as regards the yield of thiocarbimide, resemble on the whole the experiments with dibenzylthiocarbamide. Although an acetylated derivative is no doubt first formed, I have not yet separated it from the accompanying ethylacetamide.

The diethylthiocarbamide was prepared directly from ethylamine and ethylthiocarbimide.

Yields of Ethylthiocarbimide from Diethylthiocarbamide at the Boiling Point of Acetic Anhydride.

Quantities used, 6·6 grams of $CS(NH{\cdot}C_2H_5)_2$ and 10·2 grams $(CH_3{\cdot}CO)_2O$.

Theoretical yield of $C_2H_5{\cdot}NCS$, 4·35 grams.

The thiocarbimide was estimated by conversion into ethylthiocarbamide.

	Time.	Weight of the thiocarbimide.	Percentage of theoretical.
Exp. 41.	10 minutes.	0·75 gram.	17·24 per cent.
" 42.	30 "	1·77 "	40·68 "
" 43.	50 "	2·02 "	46·58 "

Want of material prevented me from carrying the experiments further, and they are so far incomplete, as the fall in the yield of mustard oil has not yet been reached.

A summary of the results arrived at in the present investigation may be stated as follows:—

When the *symmetrical bisubstituted aromatic* thiocarbamides are heated with acetic anhydride—

1. No acetylated derivative of the thiocarbamide is produced.
2. The mere dissolution of the thiocarbamide in the anhydride is accompanied by simultaneous decomposition into an "anilide" and a thiocarbimide in accordance with the equation

$$CS(NHR)_2 + (CH_3{\cdot}CO)_2O = R{\cdot}NCS + CH_3{\cdot}CONHR + CH_3{\cdot}COOH.$$

3. *Five minutes* heating at the boiling point of acetic anhydride gives an almost theoretical yield of the thiocarbimide.
4. An extension of the time of heating induces secondary reaction between the thiocarbimide and acetic acid, whereby the yield of the former is diminished,

$$RNCS + CH_3\cdot COOH = CH\cdot CONHR + COS.$$

In the case of the *fatty* thiocarbamides—

1. A well-defined acetylated thiocarbamide is first produced.
2. Further heating gives rise to the formation of a thiocarbimide, but the yield of the latter is not high, on account of the secondary action proceeding simultaneously with the generation of the thiocarbimide.
3. Prolonged heating gives a substituted amide as final product, the result of three distinct actions.

University Laboratory, Trinity College, Dublin.

XLV.—CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Action of Alkalis on the Nitro-compounds of the Paraffin Series. Formation of Isoxazoles.

By Professor WYNDHAM R. DUNSTAN and T. S. DYMOND.

IN 1888 we communicated to the Society (Proc., 1888, 117) a preliminary account of a remarkable reaction which we had observed to occur when nitroethane is warmed with aqueous solutions of alkali carbonates or hydroxides. The reaction was first observed in the autumn of 1887, when we had occasion to prepare some quantity of ethyl nitrite and nitroethane by acting on silver nitrite with ethyl iodide. The nitroethane was dried by digestion with, and distillation from, potassium carbonate, and after nearly all the nitroethane had been obtained, an aromatic oily substance (C_6H_9NO) passed over into the distillate. The brownish residue contained potassium nitrite. We could find no record of this reaction having been previously observed, and it soon became evident that the aromatic body belonged to a new class of organic compounds. We learned subsequently that the Russian chemist Sokoloff was also engaged in examining the action of alkalis on the paraffinic nitro-compounds, and that he had communicated an account of his experiments to the Russian Chemical Society (*J. Russ.*

Chem. Soc., 1887, 374; 1888, 498). Sokoloff had isolated and partly examined the new compound which he had produced by heating nitroethane with alcoholic ammonia in closed tubes. On comparing Sokoloff's results with those we had obtained, it became evident that he had not completely examined the nature of the reaction, and had, as we shall proceed to show, overlooked one of the most important products, namely, acetonitrile. Moreover, he does not appear to have investigated the constitution of the new compound. We therefore decided to continue the enquiry, and we now have the honour to lay before the Society a full account of the work we have done up to the present time. We have fully examined the products of the action of alkalis on nitroethane, and have investigated the properties and modes of decomposition of the new compound which results from this action. We have also succeeded in ascertaining the constitution of this substance, and in effecting its synthesis by an entirely independent reaction. In addition, preliminary experiments have been made with nitromethane, nitropropane, and other nitro-derivatives belonging to the same series.

I.—ACTION OF ALKALIS ON NITROETHANE.

Action of Alkali Carbonates and Hydroxides.

Dry potassium carbonate is without action on dry nitroethane. When, however, nitroethane is allowed to stand with a strong aqueous solution of potassium carbonate, the mixture becomes yellow, and potassium hydrogen carbonate separates in crystals. On warming the mixture, it darkens, and carbon dioxide is evolved. A brownish-yellow oil, corresponding with about one-third of the nitroethane taken, remains on the surface of the solution, which now contains abundance of nitrite and a little ammonia, but no nitrate. If the mixture has been warmed for some hours, the whole of the nitroethane is decomposed, and no further change occurs on boiling. The oily layer, after having been dried with potassium carbonate, may be separated by fractional distillation into two parts. A fraction is obtained, boiling between 75° and 80°, and a second large fraction between 160° and 170°; a brown, resinous substance remains undistilled. By repeated distillation, the first fraction is resolved into a liquid boiling between 77° and 81°, which possesses all the properties of *acetonitrile*. It burns with a crimson flame, and is decomposed by ebullition with acids and alkalis, in the latter case with the evolution of ammonia. The acetonitrile was evidently contaminated with a trace of some substance which lowered its boiling point. To remove this impurity, it was distilled from a crystal of potassium dichromate and a few drops of dilute sulphuric acid. The purified liquid now boiled at 81°, which is the boiling point of acetonitrile. Since the quantity obtained was too small for ultimate analysis, proof of its identity with acetonitrile was obtained by heating it with aqueous alkali and isolating the product of hydrolysis. As soon as the evolution of ammonia had ceased, the alkaline liquid was neutralised with dilute nitric acid, evaporated, and decomposed with silver nitrate. The resulting silver salt was crystallised from water and analysed. It contained 63·4 per cent. of silver; calculated for $AgC_2H_3O_2$, 64·6 per cent. The acetonitrile appears to constitute about 20 per cent. (by volume) of the liquid resulting from the action of potassium carbonate on nitroethane. A little is decomposed by the alkali during the reaction, and this probably accounts for the small quantity of ammonia which is invariably formed.

The higher fraction of the original liquid consists of the new compound. Its properties will be fully described in a later section of this paper.

The amount of potassium nitrite formed in this reaction has been carefully estimated. It constitutes 16·2 per cent. of the resulting products, that is to say, one-half of the nitrogen of the nitroethane appears in this form.

Sodium carbonate, like potassium carbonate, is decomposed by nitroethane even in the cold, with the production of sodium nitroethane and carbon dioxide, which forms sodium hydrogen carbonate with the excess of the carbonate. On warming, action proceeds further, with formation of *sodium nitrite*, *acetonitrile*, and the *new compound*.

The ability of nitroethane to decompose alkali carbonates even in the cold does not appear to have been previously noticed.

Warm aqueous soda and potash rapidly convert nitroethane into potassium nitrite, the new compound, ammonia, acetic acid, and a quantity of brown resin; the ammonia and acetic acid resulting from the hydrolysis of the acetonitrile which is first formed. Alcoholic potash and soda also produce the new compound from nitroethane. Aldehyde is simultaneously formed, together with nitrite and the brown resin. Calcium hydroxide does not act on nitroethane.

Action of Ammonia.

Formation of Ammonium Nitroethane.

No ammonium analogue of sodium nitroethane has hitherto been obtained. While examining the action of ammonia on nitroethane, it was found that at 0° dry ammonia readily united with nitroethane to form a crystalline compound. Some difficulty was experienced in determining the exact composition of this substance, since, although it does not quickly melt at ordinary temperatures, loss of ammonia occurs even when it is being dried in the cold. The following method of preparing the compound for analysis proved successful. Nitroethane was mixed with about four times its volume of dry ether; the mixture was cooled to about —20°, and dry ammonia gas passed through it until crystals ceased to form. The crystals were then rapidly collected with the aid of a pump, and quickly washed with ice-cold dry ether. They were then thrown out on a piece of paper, and when the ether had completely evaporated, were transferred to a weighed stoppered bottle.

The snow-like mass of tabular crystals is almost neutral to litmus, but on standing at the ordinary temperature it slowly loses ammonia.

The cold, aqueous solution is at first only very faintly, if at all, alkaline, but by degrees ammonia is set free. The composition of the substance was ascertained by titrating an aqueous solution with dilute sulphuric acid (1100 c.c. = H_2SO_4), which slowly combines with the ammonia and liberates nitroethane.

Weight of substance taken	1·751 grams.
Standard sulphuric acid required .	10 c.c.
Ammonia in compound..........	17·6 per cent.
Calculated for $C_2H_4(NH_4)NO_2$....	18·4 „ .

When the crystals are heated, they decompose into ammonia and nitroethane, but in the absence of water no condensation occurs, even when the experiment is made at 100° in a closed tube.

Aqueous ammonia and aqueous ethylamine act on nitroethane much less energetically than potassium and sodium carbonates. When strong aqueous ammonia is used, change occurs very slowly; indeed, it is necessary to heat the mixture in closed tubes at 110—120° in order to complete the reaction. The products are ammonium nitrite, acetonitrile, and the new compound. Alcoholic ammonia has a similar effect, producing aldehyde in addition to these substances.

Physical and Chemical Properties of the New Compound.

The new compound obtained in the manner above described is a colourless liquid, having a relative density of 0·986 at 15°/15°. It boils at 171° (corr.) with slight decomposition, forming a resinous substance, and slowly darkens when exposed to light.

Distilled under reduced pressure (250 mm.), about one-half came over between 134° and 135°; this fraction had a relative density of 0·9956 at 4°/4°, 0·9859 at 15°/15°, 0·9788 at 25°/25°. The remainder of the liquid distilled between 135° and 136·5°, and its relative density was 0·9956 at 4°/4°, 0·986 at 15°/15°, 0·9788 at 25°/25°. The correspondence in the densities of the two fractions proves that the liquid is a single substance. When super-cooled, it freezes to a mass of crystals which melt at 3·5°.

On combustion, the substance afforded the following data, the carbon and hydrogen being determined in a current of oxygen, and the nitrogen by burning with copper and copper oxide in a Sprengel vacuum.

I. Substance taken, 0·1978 gram; H_2O found, 0·1504 gram; CO_2 found, 0·4633 gram.

II. Substance taken, 0·3840 gram: N_2 found, 40 c.c. at 17° and 764 mm

		Calculated for C_6H_9NO.
C	63·9 per cent.	64·8 per cent.
H	8·4 ,,	8·1 ,,
N	12·15 ,,	12·6 ,,

The molecular weight was determined by Raoult's method with acetic acid and benzene as the solvents. The following results were obtained:—

Benzene as the Solvent.

Wt. of substance	0·1322 gram.
Wt. of solvent	10·1446 ,,
Freezing point of solvent	5·833°
Freezing point of solution	5·25°
Depression for 1 gram of substance to 100 grams of solvent	0·447°

Molecular depression of benzene, 49; hence molecular weight of substance, $\frac{49}{0·447}$ = 109·5. Calculated for C_6H_9NO, 111.

Acetic Acid as the Solvent.

Wt. of substance	0·134 gram.
Wt. of solvent	12·9416 ,,
Freezing point of solvent	14·65°
Freezing point of solution	14·3°
Depression for 1 gram of substance to 100 grams of solvent	0·338°

Molecular depression of acetic acid, 39; hence molecular weight of substance, $\frac{39}{0·338}$ = 115. Calculated for C_6H_9NO, 111.

We are indebted to Dr. Perkin and to Dr. Gladstone for having determined the magnetic rotation and the refractive indices of this compound.

Magnetic Rotation.

Relative densities, 0·9953 at 4°/4°; 0·9856 at 15°/15°; 0·9784 at 25°/25°.

		Rotations.	
	t.	Sp. rot.	Mol. rot.
	15·5°	1·0879	6·809
	15·5	1·0824	6·775
	14·7	1·0824	6·786
	14·7	1·0864	6·796
	20·0	1·0837	6·806
	19·5	1·0823	6·794
	19·5	1·0823	6·794
Average ..	17·0	1·0837	6·792

Dr. Perkin remarks that the calculated value for the formula C_6H_9NO is about 6·278, which is 0·514 lower than that actually found; this might indicate that the compound is unsaturated to the extent of four equivalents of hydrogen (H_4).

Specific Refraction.

						Found.		Calculated.	
Temp.	Rel. dens.	μ_A.	μ_F.	μ_G.	μ_H.	R_A.	R_{H-A}.	R_A.	R_{H-A}.
20·5	0·9802	1·4473	1·4608	1·4673	1·4733	50·65	2·95	50·8	2·92

The refractive indices, μ, have been determined for the lines A, F, G, and H. The molecular refraction, R, is given for the line A, and also the difference (molecular dispersion) between this number and that indicating the molecular refraction for the line H. The calculated values have been obtained on the supposition that the compound is unsaturated, the lower value for oxygen being taken, and the nitrogen reckoned as having the same value as in nitriles. The usual addition has been made of 2·2 for doubly-linked carbon for the line A, and of 3 for the line H. The correspondence between the observed and calculated molecular refraction and dispersion is remarkable.

The liquid has no action on a ray of polarised light. It dissolves sparingly in water, and distils with it. Alcohol, ether, chloroform, benzene, and light petroleum dissolve it freely. It has feebly basic properties, but is without action on litmus. Acids, if not too dilute, dissolve it and the resulting solutions have not the characteristic aromatic smell of the original liquid. These salt-solutions are decomposed by the addition of water, and on heating the solutions the original substance distils with the water. When dry hydrochloric acid gas is led into the well-cooled substance, a crystalline hydrochloride, C_6H_9NO,HCl, is formed. When auric chloride is added to a solution of the hydrochloride, a crystalline precipitate is obtained, if the solution does not contain a large excess of hydrochloric acid. These crystals are best prepared by mixing aqueous solutions of gold chloride and the original substance. They contain 45·4 per cent. of gold, and are therefore a compound of the original substance with gold chloride. The formula $C_6H_9NO,AuCl_3$ requires 45·1 per cent. of gold, which agrees well with the number found. An unstable platinochloride can also be obtained.

A characteristic reaction of the substance is the formation of a crystalline compound with mercuric chloride. When an aqueous solution of this salt is added to an aqueous solution of the substance, a white, crystalline, sparingly soluble precipitate is produced. This compound is difficult to dry without losing a little of the base. A specimen dried on a porous tile over calcium chloride contained 51 per cent. of mercury; calculated for $C_6H_9NO,HgCl_2$, 52 per cent. The base slowly volatilises from the compound when it is exposed to air, and the aqueous solution is completely decomposed when heated, the base distilling over with the water. The preparation of this compound constitutes an excellent method of identifying and purifying the base, the washed precipitate being distilled with water, when nearly the whole of the base condenses with the first portions of the steam, and floats as an oil on the surface of the liquid, from which it may readily be separated, and the small quantity which remains dissolved can be extracted with ether. By carefully distilling an ethereal solution, the whole of the ether may be removed, and a residue of the pure base obtained. The base has no action on a hot solution of silver nitrate even in the presence of ammonia, nor does it form a derivative with either hydroxylamine or phenylhydrazine. Nitrous acid does not attack it, and it does not give the Liebermann reaction with phenol and sulphuric acid. No compound with picric acid could be obtained, and the pine-splinter reaction gives no coloration. Acetyl and benzoyl chlorides are without action on the base even when heated with it.

From these reactions, it may be inferred that the nitrogen in the compound is not present in the form of a nitro- or nitroso-group, nor as amidogen. The substance does not appear to be a pyrrol derivative, an aldehyde, a ketone, or a hydroxyl derivative. It is isomeric with acetopropyl cyanide and also with "acrolein-ammonia," to which, however, it bears no resemblance. In order to obtain further knowledge of its constitution, its behaviour when heated with acids and alkalis was studied, and its oxidation and reduction products were examined.

ACTION OF ALKALIS AND ACIDS.

The alkali carbonates are without action on the compound, even at its boiling point. Concentrated solutions of ammonia and potash fail to dissolve it. Heated with strong potash for some hours in a closed tube at 100—120°, some darkening occurs, but nearly the whole of the compound may be recovered unchanged. With alcoholic soda, in a closed tube at 180°, there is a little action, and a small quantity of ammonia and acetic acid are produced.

In order to ascertain whether the compound is hydrolysed or otherwise attacked by strong acids it was dissolved, in concentrated hydrochloric acid, and the liquid heated for one hour in a closed tube at 100°. No effect having been produced, the temperature was raised to 130°, and the heating continued for 48 hours. Slight darkening occurred, but on distilling the liquid with water the greater part of the substance was recovered unchanged, together with a little acetic acid. Evaporation of the remaining acid solution left a small residue, consisting chiefly of ammonium chloride, together with a minute amount of a hydrochloride soluble in absolute alcohol. This was evidently the salt of a feeble base, since, on boiling it with water, some of the base was volatilised. We have not yet succeeded in obtaining sufficient of this compound, which has a characteristic odour, for examination. It is formed in small quantity by the action of dehydrating agents on the original substance.

Ordinary nitric acid dissolves the compound with formation of an unstable nitrate which is decomposed on dilution with water. When the solution in nitric acid is heated, oxidation occurs, but without the previous formation of a nitro-compound. All attempts to prepare a nitro-compound failed. Cold fuming nitric acid dissolves the substance, but on adding water the base is regenerated.

OXIDATION PRODUCTS.

Oxidation by Potassium Permanganate.

A solution of potassium permanganate at once attacks the substance. 5 grams of the liquid were oxidised by warming with a slight excess of permanganate, and the filtered liquid was acidified with dilute sulphuric acid and distilled. An acid smelling like acetic acid passed over, and towards the end of the operation, when the liquid became concentrated, *nitric acid* distilled. The distillate was neutralised and evaporated, when potassium nitrate crystallised. The remaining liquid, mixed with silver nitrate, yielded a crystalline silver salt, which was proved by analysis to be *silver acetate*. It contained

64·5 per cent. of silver; silver acetate contains 64·6 per cent. By evaporating the liquid which had yielded these crystals, a further quantity was obtained, which was also proved to be silver acetate. No other acid could be detected either in this solution or in the liquid which remained after distillation.

Oxidation by Nitric Acid.

Warm nitric acid oxidised the compound, nitrous fumes being evolved, together with traces of hydrogen cyanide. As soon as action had ceased, the liquid was cooled, when crystals of *oxalic acid* separated. On distillation, *acetic acid* was obtained, and recognised by conversion into the silver salt, which contained 64·8 per cent. of silver, the calculated quantity being 64·6 per cent. No silver salt other than the acetate was formed, the last fraction of crystals containing 64·5 per cent. of silver. No formic acid could be detected.

Unsuccessful attempts were made to obtain intermediate oxidation products by the limited action of permanganate and nitric acid, and also by the action of silver oxide.

REDUCTION PRODUCTS.

Reduction by Heated Zinc.

Six grams of the liquid were reduced by distillation over zinc-dust heated to low redness in a combustion tube, provided first with a bulb for collecting liquid products, and secondly with a gas burette filled with mercury to receive the considerable quantity of gaseous product. There condensed in the bulb about 3 c.c. of an almost colourless liquid having an alkaline reaction. The alkalinity was proved to be due for the most part to *ammonia*. The greater part of the liquid distilled rather below 100°, and this was repeatedly fractionated, the portions boiling between 75° and 85° being finally distilled from phosphoric oxide. The liquid now boiled constantly at 80—81°, and possessed all the properties of *acetonitrile*. Proof that it was this substance was obtained by hydrolysis with potash; ammonia was evolved, whilst the remaining liquid afforded a silver salt, which was shown by analysis to be silver acetate, with which it exactly corresponded in its chemical properties. The amount of silver found by analysis was 65·3 per cent., the calculated quantity for silver acetate being 64·6 per cent.

Besides acetonitrile, a small quantity of a weak base resulted from the reduction. The gas which had been collected was a mixture of methane, ethane. and hydrogen.

Reduction by Metal and Acid.

The compound is remarkable for the manner in which it withstands the attack of the usual reducing agents.

To a mixture of tin and hydrochloric acid, from which hydrogen was being briskly evolved, 5 grams of the substance was gradually added. After action had continued for some hours, the liquid was diluted with water and distilled. Nearly the whole of the substance was recovered. In other experiments the compound was dissolved in concentrated hydrochloric acid, and small pieces of tin added from time to time. Under these conditions also there was but little change; a small quantity of ammonium chloride was produced, but the greater part of the substance was unattacked.

A mixture of the substance with somewhat diluted sulphuric acid and granulated zinc, allowed to stand for some days, led to no better result, a little ammonia and acetic acid being formed.

When zinc-dust was added in small quantities at a time to a mixture of the compound with diluted sulphuric acid, rather more action occurred; ammonia and acetic acid were produced, together with a substance, probably an alcohol, of which sufficient could not be obtained to enable it to be identified. Amalgamated aluminium foil (prepared by immersing the foil in solution of mercuric chloride) was next tried as a reducing agent. In the absence of acid, it acted extremely slowly, but after some days' contact with a warm aqueous solution of the compound, some reduction had occurred. *Ammonia* and *acetic acid* had been formed, together with what appeared to be *secondary butyl alcohol*, but the amount of substance produced was insufficient for analysis. Amalgamated aluminium acted more rapidly in presence of dilute sulphuric acid, and here again ammonia, acetic acid, and a liquid having the properties of secondary butyl alcohol were produced, but, as in the previous experiment, enough of the alcohol could not be obtained to render analysis possible.

Reduction by Hydriodic Acid.

The substance was dissolved in an excess of concentrated hydriodic acid, a little amorphous phosphorus added, and the mixture heated at 50° in a closed tube for 17 hours; no change occurred. The temperature was then raised to 100°, and the heating continued for one hour. No change being produced, the mixture was heated at 180°, but without effect. After having been exposed to the higher temperature of 200° for some hours, the contents of the tube were diluted with water and distilled. A considerable quantity of the original compound was recovered unchanged. Some action had, however, occurred, since ammonium iodide was detected in the aqueous liquid, but the other decomposition products were not formed in sufficient quantity to enable them to be separated and identified Among them was the feeble base which we have already referred to as originating in the action of strong acids and dehydrating agents on the compound.

Reduction by Sodium.

Sodium amalgam has very little action either on an aqueous or on an alcoholic solution of the substance; the nitrogen appears to be extremely slowly split off as ammonia.

By adding small pieces of sodium to an ethereal solution of the compound, standing over a small quantity of water kept below 15°, we have succeeded in effecting its reduction, and have obtained a crystalline *dihydride.* When the reduction is effected in this manner, no hydrogen is evolved, but the thin fragments of sodium acting at the juncture of the two layers become surrounded with a white, crystalline crust. If the temperature rises during the action, or if the action is too energetic, hydrogen is evolved, and the crystalline solid is decomposed with the liberation of ammonia.

The crystalline compound may be extracted from the liquid by means of chloroform, in which it is very soluble. An ethereal solution deposits well-defined, prismatic crystals melting at 110° (corr.), or they may be obtained by adding light petroleum to a solution in chloroform. The following results were afforded by the combustion of a number of different specimens of this substance:—

I. 0·1487 gram substance (crystallised from ether) gave 0·3399 gram CO_2 and 0·1340 gram H_2O.
II. 0·1262 gram substance (crystallised from ether) gave 0·2897 gram CO_2 and 0·1168 gram H_2O.
III. 0·2185 gram substance (crystallised from ether) gave 0·505 gram CO_2 and 0·2012 gram H_2O.
IV. 0·2212 gram substance (crystallised from ether) gave 0·5072 gram CO_2 and 0·2026 gram H_2O.
V. 0·1667 gram substance (crystallised from ether) gave 18 c.c. N_2 at 12° and 757 mm.
VI. 0·1526 gram substance (precipitated by light petroleum from a solution in chloroform) gave 0·3551 gram CO_2 and 0·1488 gram H_2O.
VII. 0·1542 gram substance (precipitated by light petroleum from a solution in chloroform) gave 0·3594 gram CO_2 and 0·1510 gram H_2O.

	Found.							Calculated for $C_6H_{11}NO$.
	I.	II.	III.	IV.	V.	VI.	VII.	
C..	62·34	62·60	63·03	62·53	—	63·46	63·56	63·71 per cent.
H..	10·01	10·28	10·23	10·17	—	10·83	10·88	9·73 „
N..	—	—	—	—	12·75	—	—	12·39 „

The molecular weight of this dihydride was determined by Raoult's method, using benzene as the solvent.

	I.	II.	III.
Wt. of substance	0·0476	0·0405	0·0899 gram.
Wt. of solvent	5·3795	5·670	5·670 „
Freezing point of solvent....	5·59°	5·59°	5·59°
Freezing point of solution....	5·20°	5·275°	4·90°
Depression for 1 gram of substance to 100 grams of solvent	0·440°	0·441°	0·435°
Mol. depression of benzene ..	49	49	49
Mol. wt. of substance........	111·3	111	112·6

Mean of the three determinations .... 111·6
Calculated for $C_6H_{11}NO$ .... 113·0

The crystals dissolve readily in alcohol and chloroform, less readily in light petroleum. Cold water dissolves them slowly, hot water more quickly, but with some decomposition and evolution of ammonia. The aqueous solution is faintly alkaline to litmus, and produces with mercuric chloride an abundant white precipitate. Picric acid does not precipitate the solution, which also fails to give the pine splinter reaction for pyrrol. Alkalis and acids at once decompose the aqueous solution, in the former case with abundant production of ammonia.

On heating with water in a closed tube at 100°, the dihydride is decomposed into *ammonium acetate* and *methyl ethyl ketone* in accordance with the equation $C_6H_{11}NO + 2H_2O = CH_3\cdot CO\cdot ONH_4 + CH_3\cdot CO\cdot C_2H_5$. The ketone was identified by its boiling point (76—78°) and its single oxidation product, acetic acid; on oxidation with chromic acid, the distillate, after saturation with silver oxide, afforded pure silver acetate, the solution being fractionally crystallised, and the first and last fractions analysed with the following results:—

> Percentage of silver in first fraction of salt, 64·1; percentage of silver in last fraction, 64·7; percentage of silver in silver acetate, 64·7.

The ammonium acetate was characterised by conversion into the silver salt, which was found to contain 64·3 per cent. of silver.

ACTION OF PHOSPHOROUS AND PHOSPHORIC CHLORIDES.

Phosphorous chloride does not attack the compound, even when strongly heated with it.

Phosphoric chloride does not react in the cold, but when the mixture is heated at 100° a complicated reaction ensues, hydrogen chloride is evolved, and phosphorous chloride distils, together with a mixture of chloro-derivatives. A considerable quantity of resin and some ammonium chloride are also produced. One of the chloro-derivatives is an oily liquid, having a most irritating effect on the eyes and mucous membrane of the nose. It distilled with steam, but could not be distilled alone without decomposition, even under reduced pressure. This compound contained 25·1 per cent. of chlorine, and is therefore probably a monochloro-derivative of the parent substance; the formula C_6H_5ClNO requires 24·3 per cent. of chlorine.

All attempts to replace by chlorine the single atom of oxygen which the original compound contains were failures. Although the phosphoric chloride was caused to react under various conditions, the result was always the production of chloro-derivatives containing oxygen, whilst, owing to the simultaneous occurrence of a more profound change, resin and ammonium chloride were also formed.

ACTION OF THE HALOGENS.

Dry chlorine, free from hydrogen chloride, was passed into the cooled liquid. As soon as the chlorine was no longer absorbed, the current of gas was stopped, and any free halogen the liquid might contain removed by exposure in a vacuum. No hydrogen chloride was evolved. The oily liquid had a pungent, aromatic odour. When heated, it darkened with evolution of hydrogen chloride, and even when it was distilled under reduced pressure, some change occurred, resulting in the separation of hydrogen chloride and the formation of resin. The washed and dried liquid was therefore first analysed without distillation. It contained 47·5 per cent. of chlorine. The liquid was now distilled under reduced pressure, the greater part of it was obtained near 130° (127 mm.); a little hydrogen chloride escaped. Some resin was produced, and also a small quantity of the highly irritating chloro-derivative which had been found to result from the action of phosphoric chloride. The liquid which had distilled at 130° was purified by shaking with aqueous sodium hydrogen carbonate to remove acid, the chlorine compound dissolved from the solution with ether, the ether well washed with water and dried with calcium chloride. The residue left on the distillation of the ether was then analysed. It contained 47·9 per cent. of chlorine.

The liquid resulting from the action of chlorine on the original compound therefore seems to be a mixture of two *chlorides*, a *dichloride* and a *tetrachloride*. The formula $C_6H_9NOCl_2$ requires 39·01 per cent. of chlorine; the formula $C_6H_9NOCl_4$, 56·1 per cent. These compounds are unstable, and are decomposed when heated, forming, among other substances, the pungent chloro-derivative already alluded to and ammonium chloride. The action of alkalis on these chlorides also leads to the separation of the nitrogen as ammonia.

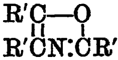
The action of bromine on the original substance is similar to that of chlorine. The addition of bromine causes the evolution of heat, but no hydrogen bromide is produced. On distilling the liquid, to which about half its volume of bromine has been added, under reduced pressure (8 mm.), the liquid, which distils near 100°, solidifies to a mass of six-sided, tabular crystals. Simultaneously hydrogen bromide is slowly formed, and a pungent, tear-exciting oil passes into the distillate. It was not found possible to recrystallise the solid from any solvent; the crystals were, therefore, washed with ether and analysed. They contained 52 per cent. of bromine, and were, therefore, probably an impure *dibromide* of the original substance. The formula $C_6H_9NOBr_2$ requires 58·9 per cent. of bromine. On heating this bromide with water, it was converted into a highly irritating bromo-derivative (C_6H_8BrNO ?), closely resembling the chloro-derivative which has already been described; resin and ammonium bromide were also formed.

The results obtained by acting on the compound with chlorine and bromine leave no doubt as to its ability to form additive compounds with the halogens, and prove it to be an unsaturated compound.

Owing to the very great difficulty of obtaining satisfactory evidence of the purity of these unstable halogen compounds, the formulæ we have suggested above require further confirmation. The complete investigation of the complicated reactions with chlorine, bromine, and phosphoric chloride, which in this case acts like the halogens, would need much larger quantities of material than we have had at our disposal.

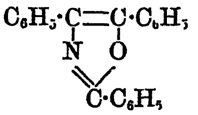
Constitution of the Compound.

The reactions of the compound are opposed to the view that it is a pyridine or pyrrol derivative, and they do not correspond with those of a keto-cyanide, acetopropyl cyanide, or propionylethyl cyanide; these compounds dissolve in ammonia, and are readily and completely hydrolysed by fixed alkalis, the acetopropyl compound yielding ammonia together with acetic and butyric acids, and the propionylethyl compound, ammonia and propionic acid. The properties of the substance point to the conclusion that the nitrogen, as well as the oxygen, forms part of a closed ring of carbon atoms. When we first made this inference from our experimental results, no paraffinic representatives of this class of compounds, the oxazoles,

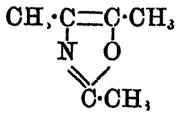


$\begin{array}{l}R'C\text{—}O\\ \;\;\|\quad\;\;|\\ R'CN{:}CR'\end{array}$,

had been prepared, although benzene derivatives having this constitution had been obtained and investigated, among other workers, by Japp and his *collaborateurs*. The phenyl analogue of the nitro-ethane derivative, assuming it to be an oxazole, is the "benzilam" of Laurent, the true formula and constitution of which was established by Japp,

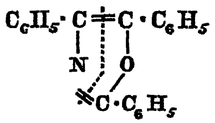


Triphenyloxazole (Benzilam).

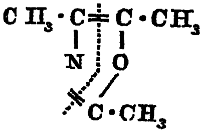


Trimethyloxazole.

A remarkable resemblance may be traced in the characters of benzilam and those of our compound. On oxidation, benzilam yields benzoic acid, whilst the new compound yields acetic acid. Both substances are distinguished by their great stability, being almost unacted on by strong acids and alkalis. The reduction products of benzilam do not appear to have been investigated, but, like our compound, it seems to be very difficult to attack. From its constitution, it may be inferred that if it were reduced the nitrogen would appear as an amine, probably as benzylamine, whilst under similar conditions our compound might be expected to yield ethylamine. The line through the formulæ indicates the direction that the change would probably take.*



Reduction of triphenyloxazole.



Reduction of trimethyloxazole.

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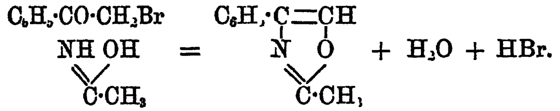
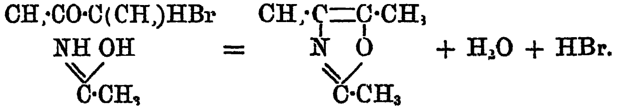
* The results which Schatzmann (*Annalen*, 261, 7) has just published on the reduction of the thiazoles, confirm the correctness of this inference.

We have carefully searched for an amine among the reduction products of our compound, but have not been able to detect a trace of such a substance. The nitrogen is separated exclusively as ammonia. We must, therefore, conclude that although the compound is closely allied to, it is nevertheless distinct from the oxazoles. The recent work of Hantzsch and the Zurich School on these compounds has since made it possible for us to devise a method of preparing trimethyloxazole, and to show that it is not identical with our compound. Lewy (*Ber.*, 21, 925) has shown that methylphenyloxazole may be obtained by heating bromacetophenone with acetamide :—



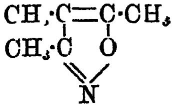
Bromacetophenone. Acetamide. Phenylmethyloxazole.

It follows from this that bromethyl methyl ketone should react with acetamide, forming trimethyloxazole :—

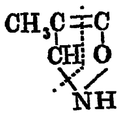


Bromethyl methyl ketone. Acetamide. Trimethyloxazole.

Brom-ethyl methyl ketone was prepared by oxidising secondary butyl alcohol with chromic acid. The resulting ketone was purified by means of its hydrogen sodium sulphite compound. The calculated amount of bromine was added in small portions to a weighed quantity of the ketone. Action rapidly occurred, the bromine being decolorised and hydrogen bromide evolved. The bromo-derivative was dissolved out with ether, and the solvent removed by distillation. The bromo-derivative, which cannot be distilled under ordinary pressure without decomposition, was heated with excess of acetamide in a closed tube at 120—130° for one hour. The contents of the tube were distilled with water, when a liquid was obtained having feebly basic properties, and in many other respects resembling the nitroethane derivative, but differing entirely from it in its odour and physical properties. Crystalline compounds with mercuric chloride and auric chloride were obtained. Since the base was not identical with our compound, its properties were not further examined.

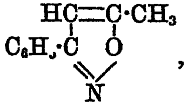
The behaviour of the nitroethane derivative on reduction suggests that its molecular constitution differs from that of an oxazole in containing oxygen in union with nitrogen. The formula 

correctly summarises all the reactions of the substance, its feebly basic properties, its ability to combine directly with hydrogen and with the halogens, its oxidation to acetic acid by permanganate, and to acetic and oxalic acids by nitric acid, and also the formation of ammonia and secondary butyl alcohol on reduction, as well as the remarkable hydrolysis of the dihydride into ammonium acetate and methyl ethyl ketone, when the "ring" is split in the direction indicated by the line which has been drawn through the formula :—



The production of secondary butyl alcohol on reduction is, of course, due to the hydrogenation of this ketone. The molecular refraction and magnetic rotation of the original substance do not help us to adopt this formula, chiefly because these properties have not been examined in other bodies of similar constitution: so that no data exist for comparison. They are, however, not inconsistent with this view of the structure of the compound, and they do distinctly confirm the existence of unsaturated carbon which this formula assumes.

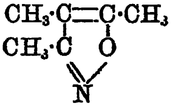
SYNTHESIS OF THE COMPOUND FROM METHYLACETYLACETONE.

When we commenced this inquiry, no compound having this constitution had been obtained, either in the paraffin or benzene series, but, more recently, Claisen (*Ber.*, **21**, 18) has described a substance produced by the dehydration of the hydroxime of benzoylacetone, to which he has assigned the formula 

, and classified as a monazole.

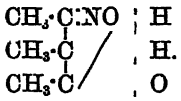
But neither in this communication nor in later papers by Claisen's pupils (Zedel, *Ber.*, **21**, 2178), is any information given about the reactions of these compounds. Their oxidation and reduction products do not appear to have been studied, and the constitution assigned to them is supported almost entirely by evidence derived from synthetical experiments. We were, therefore, unable to ascertain how far the reactions of our compound corresponded with those of the substance obtained by Claisen. Accepting as correct Claisen's inferences as to the mode of production of the monazoles from the symmetrical β-diketones, we attempted to prepare the derivative of nitroethane by a reaction analogous to that by means of which he obtained phenylmethylmonazole* or phenylmethylisoxazole, namely, by the action of hydroxylamine on methylacetylacetone (diacetylethane), which should, *ex hypothesi*, lead to the formation of our compound, if it were trimethylisoxazole. The reaction may be represented as occurring in two stages: the first, in which the monhydroxime of the diketone is produced, and the second, in which this hydroxime undergoes dehydration.

(i) $CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}CO{\cdot}CH_3 + NH_2OH =$
Methylacetylacetone.
$CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}C(CH_3){:}NOH + H_2O$;

(ii) $CH_3CO{\cdot}CH(CH_3){\cdot}C(CH_3){:}NOH = H_2O +$  ;
Methylacetylacetonoxime.

Trimethylisoxazole.

or more graphically



Dehydration of monhydroxime.

Acetylacetone was prepared by Claisen's method (*Ber.*, **22**, 1014), a mixture of ethyl acetate and acetone being decomposed with sodium,

$$CH_3{\cdot}CO{\cdot}O{\cdot}C_2H_5 + CH_3{\cdot}CO{\cdot}CH_3 + Na = CH_3{\cdot}CO{\cdot}CHNa{\cdot}CO{\cdot}CH_3 + C_2H_5{\cdot}OH.$$

The sodium acetylacetone thus obtained was converted into the insoluble, purple copper salt, which was collected, washed, and the diketone liberated from it by the addition of diluted sulphuric acid. The compound was extracted with ether, and then distilled from the solution after it had been dried with calcium chloride. The acetylacetone boils, apparently with slight decomposition, at 136°.

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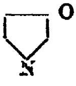
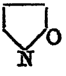
* The nomenclature which has since been suggested by Hantzsch (*Annalen*, **249**, 1) for compounds containing this nucleus seems to us more expressive and convenient. We shall, therefore, adopt it in this paper. Compounds containing the group  are termed oxazoles, and those containing the nucleus  isoxazoles.

In order to convert this substance into its methyl derivative, the sodium compound was heated with methyl iodide in closed tubes at 140°. The resulting methylacetylacetone was purified by fractional distillation. It is a colourless liquid, having a slightly aromatic odour, boiling at 169°. To its alcoholic solution was added an alcoholic solution of hydroxylamine hydrochloride. Reaction immediately occurred with rise of temperature. The mixture was heated for a short time at 100°, then largely diluted with water, and distilled. There passed over with the steam a liquid which was at once recognised as the derivative we had obtained from nitroethane by the action of alkalis. After purification by conversion into its compound with mercuric chloride, it boiled at 171° (corr.), and was identical in all its properties with the nitroethane derivative. On analysis, it yielded data corresponding with those deduced from the formula C_6H_9NO.

I. Substance taken, 0·0444 gram; H_2O obtained, 0·0348 gram; CO_2 obtained, 0·1054 gram.

II. Substance taken, 0·2986 gram; N obtained, 31·6 c.c. at 10° and 762·3 mm.

	Found.	Calculated for C_6H_9NO.
C	64·7 per cent.	64·8 per cent.
H	8·7 ,,	8·1 ,,
N	12·69 ,,	12·7 ,,

This synthesis confirms the view of the constitution of the substance which we had inferred from its reactions, and satisfactorily establishes its identity with trimethylisoxazole. By the action of hydroxylamine on methylacetylacetone, besides trimethylisoxazole, *acetonitrile* was formed. It was separated from the oxazole by fractional distillation and hydrolysed by alcoholic potash in the usual manner. Ammonia was produced, together with a volatile acid, which was proved by the analysis of its silver salt to be acetic acid, the percentage of silver found being 64·28.

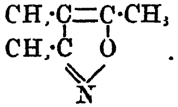
The formation of the nitrile in this reaction may be accounted for by supposing that an acetyl group is eliminated as aldehyde, which would be converted into acetalhydroxime by the hydroxylamine. The hydroxime on dehydration would yield acetonitrile, $CH_3{\cdot}CH{\cdot}NOH = H_2O + CH_3{\cdot}CN$.

For the purposes of the foregoing discussion we have accepted as correct the constitution usually assigned to the β-diketones, which satisfactorily accounts for the usual reactions of these compounds. In the course of our work, however, we have obtained evidence which suggests the possibility that they are ring-compounds, the ring containing oxygen as well as carbon, or at all events that these compounds on some occasions act as if they were thus constituted. Further experiments are being made on this important question.

Since trimethylisoxazole is now prepared for the first time, and as the reactions of the known isoxazoles have not been fully examined, it is desirable to recapitulate here the principal properties and reactions which we have already described as belonging to the derivatives of nitroethane, which is now proved to be trimethylisoxazole.

Principal Properties and Reactions of Trimethylisoxazole.

Formula —

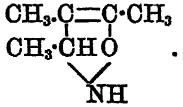


$$\begin{array}{l} CH_3\cdot C = C\cdot CH_3 \\ CH_3\cdot C \quad\; O \\ \qquad\;\; N \end{array}.$$

Modes of Formation.—By the action of alkalis on nitroethane, and of hydroxylamine on methylacetylacetone.

Boiling point....	171° (corr.)	Magnetic rotation.....	6·792
Freezing point...	3·5° (corr.)	Molecular refraction...	50·8
Relative density..	0·986 at 15°/15°	Molecular dispersion ..	2·92
Rotatory power..	None		

Mercurochloride	$C_6H_9NO,HgCl_2$
Gold chloride compound.	$C_6H_5NO,AuCl_3$
Chlorides.............	$C_6H_9NOCl_2$; $C_6H_9NOCl_4$ (?).
Bromides.............	$C_6H_9NOBr_2$.
Chloro- and bromo-derivatives............ ...	C_6H_8ClNO; C_6H_8BrNO (?).
Oxidation products	Acetic (and oxalic) acid.
Reduction products.....	Ammonia, acetic acid, secondary butyl alcohol.
Products of reduction by heated zinc	Acetonitrile, &c.
Product of hydrogenation by sodium and water..	Dihydride of trimethylisoxazole,
Hydrolytic products of the dihydride	Ammonium acetate, methylethylketone.



$$\begin{array}{l} CH_3\cdot C = C\cdot CH_3 \\ CH_3\cdot CH \;\, O \\ \qquad\quad NH \end{array}.$$

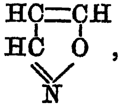
Mechanism of the Reaction between Alkalis and Nitroethane.

We have ascertained that when alkalis react with nitroethane, the products of the change are formed approximately in accordance with the proportions indicated by the equation

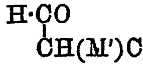
$$4C_2H_5NO_2 = C_6H_9NO + CH_3\cdot CN + 2HNO_2 + 3H_2O.$$

The occurrence of such a reaction as this between an alkali and a nitro-compound is most remarkable, and cannot be satisfactorily explained, if the usual formula for nitroethane be rigidly adhered to. By modifying the formula, in accordance with the doctrine of tautomerism, and supposing the compound to contain one or two hydroxyl groups, more than one mode of interaction becomes possible. We do not, however, now propose to discuss this question, on which much might be written by way of suggestion, until we have ascertained whether any intermediate compounds can be isolated which would throw light on the mechanism of the change. Experiments we have already made would lead us to conclude that alcohol is not one of these transition compounds, and that the acetonitrile is not produced at the expense of the isoxazole by the action either of alkali or of hydroxylamine. On the other hand, it seems possible that a derivative of a β-diketone is concerned in the transformation, this substance originating from the nitro-compound. It is a fact of much significance that, whilst alkalis act on nitroethane, forming trimethylisoxazole and acetonitrile, these same compounds result from the action of hydroxylamine on methylacetylacetone.

II. The Action of Alkalis on Nitromethane.

The action of alkalis on nitromethane is much more rapid and intense than on nitroethane, and it proceeds further. The character of the change appears to be similar. When nitromethane is mixed with aqueous *ammonia* or *potassium carbonate*, reaction is immediate, the mixture darkens, and finally becomes almost black. *Nitrite* is formed, together with *hydrogen cyanide* and a large quantity of a resinous substance. From our study of the action of alkalis on nitroethane, we should infer that nitromethane would yield isoxazole,  , the parent base of which the compound resulting from the action of alkalis on nitroethane is the trimethyl derivative. So far, however, we have not been able to isolate this interesting compound, which seems to be instantly decomposed, but our investigation of the reaction is not yet completed.

The results of the recent work of Claisen and Stock (*Ber.*, **24**, 130) on the action of hydroxylamine on benzoylacetaldehyde, renders it probable that this isoxazole, in presence of alkali, would pass into the alkali salt of the isomeric cyanacetic aldehyde,



$$\begin{matrix} H{\cdot}CO \\ | \\ CH(M')CN \end{matrix} \cdot$$

III. ACTION OF ALKALIS ON PRIMARY NITROPROPANE.

The action of alkalis on nitropropane is much weaker than on its two lower homologues. Aqueous ammonia hardly attacks this nitro-compound, even at a temperature of 100—120°, in a closed tube. Potassium carbonate solution acts slowly, and in order to completely decompose the nitropropane it is necessary to heat the mixture for some hours at 100°. On distillation, an oily liquid condenses with the steam, whilst *potassium nitrite* and *resin* remain in the residue. The oily liquid, after having been separated and dried in the usual manner, was resolved, by fractional distillation, into two substances; one of these, which was difficult to purify, finally distilled between 98° and 100°, and had all the characteristic properties of *propionitrile*. Since only a small quantity was available, its identity was established by hydrolysing it with aqueous potash, when ammonia was abundantly evolved. The resulting potassium propionate was converted into the silver salt, which was analysed in the ordinary way. It contained 59·12 per cent. of silver; silver propionate contains 59·6 per cent.

The liquid which remained after the propionitrile had distilled consisted of a body which, after fractionation, boiled at 214° (corr.). Its relative density was 0 9382 at 15°/15°.

On combustion it afforded the following data :—

	I.	II.	III.	IV.
Substance taken	0·1738 grm.	0·1656 grm.	0·2282 grm.	0·1614 grm.
CO_2 obtained..	0·4442 „	0·4212 „	0·5836 „	—
H_2O „ ..	0 1577 „	0·1438 „	0·2022 „	—
N_2 „ at 12·5°, 764 mm.	—	—	—	12 c.c.

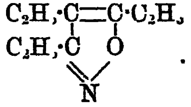
	Found.				Calculated for $C_9H_{15}NO$.
	I.	II.	III.	IV.	
C	70 2 per cent.	69·3 per cent.	69·7 per cent.	—	70·5 per cent.
H	10·08 „	9·64 „	9·84 „	—	9·8 „
N_2	— „	— „	— „	9 1	9·14 „

The molecular weight of the liquid was ascertained by Raoult's method, using acetic acid as the solvent.

	I.	II.
Wt. of substance............	0·0778 gram.	0·1556 gram.
Wt. of solvent..............	6·5378 „	6·5378 „
Freezing point of solvent	15°	15·02°
Freezing point of solution....	14·7°	14·42
Depression for 1 gram of substance to 100 of solvent....	0·258°	0·258°
Mol. depression of solvent....	39	39
Mol. weight of substance.....	151	151

The molecular weight corresponding with the formula $C_9H_{15}NO$ is 153.

The substance is thus shown to have the composition of *triethylisoxazole*, . In most of its reactions it resembles the trimethylisoxazole obtained under similar conditions from nitroethane.



We have, however, not succeeded in solidifying it, and it does not appear to form a compound with either mercuric chloride or gold chloride. In these particulars it differs from trimethylisoxazole. When oxidised with nitric acid, a volatile acid was obtained, which, by the analysis of its silver salt, was proved to be *propionic acid*. The percentage of silver in the silver salt was 59·8, the percentage of silver in silver propionate being 59·6.

The compound is somewhat more difficult to oxidise than the trimethylisoxazole, and since it was thought that it might be the dihydride of triethylisoxazole, the hydrogen being united to the two doubly-linked carbon atoms, attempts were made, by the action of silver oxide, and by the limited action of nitric acid, to oxidise these two hydrogen atoms and so to obtain triethylisoxazole. No such effect could, however, be observed. Under no circumstances was a compound produced which combined with mercuric chloride, although an intermediate oxidation product was obtained, which is being further examined.

We are indebted to Mr. A. J. Simons, one of the workers in this laboratory, for the assistance he has given us in examining the properties of this compound.

The reaction between alkalis and primary nitropropane seems to be represented by the equation

$$4C_3H_7NO_2 = C_9H_{15}NO + C_2H_5CN + 2HNO_2 + 3H_2O.$$

IV. ACTION OF ALKALIS ON SECONDARY NITROPROPANE.

The results recorded in the foregoing pages relate to the action of alkalis on primary nitro-compounds. It became of interest to determine whether a similar reaction occurs with secondary and tertiary nitro-compounds. Our observations on the behaviour of these bodies are not yet completed, but we have already noticed that secondary nitropropane undergoes a change which is, in all probability, similar in kind to that sustained by primary nitropropane, although the products of the reaction are different. Alkali *nitrite* is produced, but no triethylisoxazole. Another substance, responding to the reactions of a pseudo-nitrol, has been isolated, and is being examined.

Research Laboratory of the Pharmaceutical Society, London.

ANNUAL GENERAL MEETING,

March 25th, 1891.

Dr. W. J. Russell, F.R.S., President, in the Chair.

I AM happy to be able to report to the Fellows that the Society continues to increase and prosper. We have now 1754 Fellows, and the communications received during this year have been more numerous than in the preceding year.

The following tabular statement gives the numerical position of our Society:—

Number of Fellows (Anniversary, March 1890)		1698
Since elected and paid admission fees		114
		1812
Removed on account of arrears	28	
Withdrawn	13	
Deceased	17	
		58
Present number of Fellows		1754
Number of Foreign Members	33	
Deceased (Dr. Heinrich Will)	1	
Present number of Foreign Members	32	

The number of elections this year is less by 31 than last year, and the absolute increase in the number of Fellows during the year is 54 instead of 84.

The deceased Fellows are:—Dr. M. Bechler, W. Blythe, H. B. Brady, F.R.S., C. Innes Burton, W. Lant Carpenter, Thos. Carnelley, J. B. Hutcheson, S. A. Hill, Robert MacCalmont, E. C. Nicholson, T. R. Ogilvie, C. P. Phillips, Harry Poland, Henry Smith, W. C. Stevens, T. O. Sandell, and Henry H. Walker.

Withdrawn:—A. Bain, E. N. Butt, Joseph Barker, Robert Carruthers, W. H. Glazier, James Hall, A. E. Johnson, E. A. Parnell, W. E. Porter, W. R. Reffell, John Stokes, Arthur Taylor, and R. C. Tresider.

The financial state of the Society, I am sorry to say, is not quite so satisfactory as it has been of late. The details you will hear from the Treasurer; consequently I have only to note the fact that the receipts from subscriptions this year are £177 less than last year. This falling off is to be accounted for, firstly, by an accidental circumstance, there being this year 11 fewer life compositions than last year, and, secondly, the increase during the year of the number of candidates who have been blackballed, the exact number rejected being 26.

Much care and thought have been bestowed both by the Committee and the Librarian on the Library, and it continues to increase at a very uniform rate, and to receive all the new and valuable works on chemistry as soon as they are published. The exact increase in the number of works in each department of the Library is as follows:—

	March 25th, 1890.	Additions in 1890–91.	Present State.
Volumes of systematic works..........	3,082	122	3,204
Volumes of periodicals...............	5,667	203	5,870
Volumes of duplicate periodicals for circulation	1,135	53	1,188
Pamphlets.........................	1,450	22	1,472
	11,334	400	11,734

Compared with last year, the number of systematic works added to the Library are fewer, but the volumes of periodicals added are more numerous. With regard to the expenses of the Library, they are £120 less than they were last year.

I have no hesitation in saying that the character of the communications which the Society has this year received from the Fellows is certainly equal, if not of a higher character than on any former occasion; the actual number which have been published in the Transactions happens to be the same as it was last year, namely, 72, but whatever their character may have been, their length is considerably greater than those of last year, for they occupy 1051 pages instead of only 772. The total number of papers communicated to the Society was 101; last year it was 100. On turning to the other volume of our Journal, we find there has been, compared with last year, a considerable increase in the number of abstracts; this year 2341 appear in the Journal; last year there were 2131. This year the abstracts occupy 1527 pages; last year 1252. The increased size of the volume for 1890 has necessarily increased the cost of the Journal, which has been £413 more than it was last year.

The time has again come round for the award of the Longstaff medal. The Fellows will remember that by the trust deed the Council are instructed every third year to award the medal to the Fellow of the Society who, in their opinion, has done the most to promote chemical science by research. This instruction is one not always easy to carry out, but I am sure that the Fellows will feel that the unanimous decision of the Council to award it to Professor Japp this year is eminently satisfactory. He has, during the last three years, either alone or in conjunction with others, communicated to our Society eight papers, and all who are following the higher development of organic chemistry know how valuable to this branch of the science the carefully thought out papers of Dr. Japp have been. I only regret he is not here to receive the medal in person.

The great event of the year with regard to our Society has undoubtedly been the celebration of the Jubilee which occurred on the 24th and 25th of February. As it is an event of so recent date and, moreover, one to be recorded in detail elsewhere, I need not do more in this place than state, for the sake of future reference, the facts that a special meeting of the Society was held in the theatre of the University of London, at which three of the original founders of the Society, Sir W. R. Grove, Sir Lyon Playfair, and Mr. Heisch, were present, and that deputations congratulating the Society on attaining its 50th birthday were present from the Royal Society, the Pharmaceutical Society, the Chemical Society of France, the Berlin Chemical Society, and other societies; also that Mr. Warington presented an album containing photographs of many of the founders of the Society and letters relating to its establishment; that on the evening of the 24th the President and Council gave a *soirée* at the Goldsmiths' Hall, which was most kindly lent to them by the Worshipful Company, and that an exceedingly interesting collection of apparatus illustrative of important researches which had mostly been carried out by former Presidents of the Society was exhibited and attracted much attention. On the following day a dinner was held in celebration of the Jubilee, at which the Prime Minister, Lord Salisbury, and several other distinguished guests were present, and about 230 of the Fellows. The proceedings on each occasion proved to be of so much interest that the Council feel that a full record should be preserved, and they intend to issue in a separate form as soon as possible an account of what took place at each of the above meetings.

The suggestion I made in my report last year that a fitting memorial of the Jubilee might be a subject catalogue of the Journal from its commencement was, I think rightly, on further consideration, abandoned, the labour and expense of compiling such a catalogue being more than the result would justify.

The exhibition at an extra meeting of new forms of apparatus was held on May 8th, and proved to be of considerable interest and practical use. No discourse has this year been given to the Society.

It seems appropriate for me on the present occasion briefly to chronicle the changes which have occurred in the constitution and government of the Society since its formation. The history of these changes is, however, soon told, for with the exception of obtaining in 1848 a Royal Charter, they have been remarkably few, in fact, the evidently very carefully considered constitution and plan of government suggested when the Society was founded has in all essential points been found to work well and to accomplish the ends intended. The object of our Society is still the same as it was defined to be when it was founded, namely: "the promotion of chemistry and those branches of science immediately connected with it, by reading, discussion, and subsequent publication of original communications and the formation of a library and a museum." The museum, however, was not found to be a necessary or even advantageous adjunct to the Society, and although it certainly possessed many specimens of considerable interest and value, it was determined at a General Meeting held in 1866, that it should be given up; the donors of specimens having a right to claim their gifts, and the remaining specimens being given to institutions or individuals that might desire to have them.

During the same year that the Society obtained its Charter, another very important advance was made; that was the establishment of the Quarterly Journal. It was well edited by Dr. Ronalds, and this great improvement in the manner of issuing the records of the Society did much to raise its general status, and give it a higher position among Scientific Societies.

Little or no alteration of the bye-laws or the plan of working the Society seems to have occurred for many years.

In 1852 the number of Vice-Presidents, which then was four, was increased, by adding all past Presidents, and it is not until 1866 that there is any other change worth recording. In that year, a "new form of nomination paper for the proposal of gentlemen as Fellows of the Society" was introduced, and this seems to be the first indication of any feeling having arisen that undesirable people were seeking and obtaining election into the Society. This same subject has from time to time caused far more discussion among the Fellows than any other question relating to the government of the Society, and it is of interest and importance to note briefly the nature and results of these discussions. In order to understand fully their origin and meaning, we must bear in mind that as the Society grew and prospered, and chemistry became of more value in the arts and in matters relating to every day life, a very natural impression arose among a large portion of the public, that since all the most distinguished chemists of the day belonged to our Society, therefore, every one who was a member of it must be a thorough chemist. This misconception on the part of the public, I think, has been most mischievous, and has given rise to much of the disagreement which has occurred among the Fellows. It is impossible now to trace the exact history of the gradual development of this feeling of discontent, which certainly arose at least among some of the Fellows, but in 1867 this matter was, I can hardly say openly, discussed, because the discussion was carried on to a great extent by persons under assumed names, but was very freely discussed, principally in the pages of the *Chemical News*, the question at issue being whether undesirable persons did easily obtain admittance into the Society, and whether any but trained chemists ought to be admitted. Clearly what some desired was that the title F.C.S. should be a kind of degree, a distinction to be applied only to trained chemists. A good deal evidently of strong feeling existed at the time, and a good deal was written on the subject. The Council felt the importance of the question, and in their Report of 1867 say that they have it "under their consideration to raise the standard of qualification for the admission to the Fellowship:" they seem to have considered the matter very carefully, and also to have referred it to a sub-committee. which consisted of Mr. Crookes, Dr. Miller, Dr. Odling, Mr. Wanklyn, and Dr. Williamson. This Committee issued a Report in November, 1867, which was adopted by the Council and a copy sent to all the Fellows. This Report seems to be, even at the present time, of so much interest and so fully to state the case, that I desire to read it on the present occasion.

"CHEMICAL SOCIETY, BURLINGTON HOUSE, PICCADILLY, W.,

"*November* 11*th*, 1867.

"SIR,

"At a meeting of the Council, held on May 16th, 1867, it was resolved, 'That a Committee of five be appointed to consider the by-laws relating to the election of Fellows, Honorary Members, and Associates, and to report to the Council.' It was further resolved, 'That the Committee consist of Mr. Crookes, Dr. Miller, Dr. Odling, Mr. Wanklyn, and Dr. Williamson.'

"Upon the presentation of the Committee's report, at a meeting of the Council, held on November 7th, it was resolved, 'That this report be approved, and that a copy of it be sent to each Fellow of the Society.'

"We beg to append the report in question, and have the honour to remain,

"Your obedient Servants,
"W. Odling,
"A. Vernon Harcourt,
"*Hon. Secretaries.*

"Your Committee were appointed by a resolution, passed at a Meeting of Council, held on May 16th, 1867, in fulfilment of the intention which the Council announced to the Society in its Anniversary Report.

"As bearing upon the standard of qualification for admission to the Fellowship of the Chemical Society, your Committee, from replies they have received to a circular which they addressed to all the Fellows, and from conversations they have held with different Fellows whom they chanced to encounter, have ascertained the existence among the Fellows of the Society of two very distinct views as to its nature and purposes.

"Many Fellows appear to regard the Society as being by rights an association of eminent scientific men; and they accordingly look upon the Fellowship of the Society as a distinction which should be conferred only upon those who have given evidence of marked chemical proficiency, as, for example, by the production of some original memoir; so that the election of any one as a Fellow of the Society should stamp him at once as being a well-trained chemist and competent investigator.

"In favour of this view, it is urged that the initials F.C.S., appended to the name of any gentleman, seem to imply that his attainments have won for him a public recognition somewhat in the character of a degree; and that these initials ought to signify, in reality, that which they seem to imply, and which is indeed their proper signification.

"It is further urged that the Fellowship of the Chemical Society is essentially an honorary distinction, although from the ease with which it can be obtained, practically by any who choose, it is a distinction but little valued by the better sort. It is, however, eagerly sought after and obtained by men who are not perhaps altogether desirable—who certainly have no claim to the title of scientific chemists—and who, in some cases, do not even join the Society from any interest they take in chemical science, but solely with the view of parading a distinction to which their merits do not really entitle them.

"Moreover, from the circumstance that chemistry is pursued, not only as a science but also as a profession and trade, the right to append the intials F.C.S. possesses a sort of trade value, exceeding its cost, to mere trading or professional chemists; as suggesting that those who have the privilege of using these initials are better qualified men than their brethren who are not thus distinguished.

"From these causes, it is said, the Fellowship of the Chemical Society has gradually sunk in public estimation; and accordingly it is very desirable that something should now be done to restore, if possible, its original prestige.

"On the other hand, many Fellows are of opinion that the Society is merely an association of individuals, having joint but various interests in the progress of both pure and applied chemistry; that the object for which the Society exists is not to confer honour upon any individual whatever, but to promote the general advancement, distribution, and application of chemical knowledge; and that, as a general rule, men engaged in pursuits more or less dependent on or connected with chemistry, and taking a sufficient interest in chemistry to wish to join the Society, should, unless personally objectionable, have every facility afforded them for joining it.

"In favour of this view, the preamble to the Charter is adduced, and especially the following paragraph: whereas certain of our subjects 'did establish and are now members of a society known by the name of the Chemical Society, for the general advancement of chemical science, as intimately connected with the prosperity of the manufactures of the United Kingdom . . . ., and for a more extended and economical application of the industrial resources and sanitary condition of the community,' &c.

"It is further maintained that the Society, from its origin until the present time, has always been of a mixed rather than of an exclusively scientific character—that the present Fellows form quite as distinguished a body as have ever constituted the Society—and that many, at any rate, of the most distinguished individual Fellows do not feel themselves at all discredited by being associated as joint Fellows of the Society with men who are engaged or interested in chemical pursuits, but whose scientific or social position is inferior to their own.

"Moreover, of scientific as distinguished from purely professional societies, the Royal Society, it is urged, is the only one of which the Fellowship is conferred in recognition of eminent scientific merit—the special science societies being practically open to all students of, and workers at, their respective subjects, who may wish to be elected to their respective Fellowships. To limit the Chemical Society then to eminent scientific chemists would be tantamount to making it the chemical section of the Royal Society, instead of allowing it to have a distinct function and character of its own.

"It is further urged that the circumstance of chemistry being to some extent a profession, so far from indicating the propriety of making the Fellowship of the Chemical Society an honorary distinction, rather contra-indicates it. For, independently of the difficulty, or rather impossibility, of withholding or conferring the honour without doing much injustice to individuals, the Society, by professing to choose out the most worthy, would naturally be held responsible for its choice, and identified more or less with the acts of each and all of its Fellows.

"Your Committee, having given these different views their best consideration, are not prepared to recommend any alteration in the by-law relating to the election of Fellows, which would have the effect of confining the Fellowship of the Society to strictly scientific men.

"But they think it may be advisable, although they have failed to elicit evidence of the admission of any significant proportion of unsuitable persons into the Society, to make some modification in the present by-law, with a view to increase the security against the accidental election of undesirable candidates.

"They accordingly suggest that in future, or after a certain interval of time, the form of recommendation of a candidate, referred to in the first paragraph of the by-law in question, shall be required to be signed by five, instead of by only three, Fellows of the Society, of whom three at least, instead of only one, shall be required to sign from personal knowledge; and further, that in the second line of the printed form of recommendation, the words 'Qualification or Occupation' shall be substituted for the words 'Position, Profession, or Occupation.'

"At present your Committee are not disposed to advise any alteration in the second paragraph of the by-law, which requires three-fourths of the votes given to be in favour of the candidate, in order to effect his election. If, however, contrary to the anticipations of the Committee, any section of the Fellows should be found to make an improper use of this requirement, your Committee would then recommend that one or other of two courses should be proposed by the Council and adopted by the Society; that is to say, that the by-law should be so altered as to render valid the election by a mere majority, or else that the by-law should be temporarily abrogated, and during its abrogation the election of Fellows be delegated by the Society at large to a Committee appointed for the purpose."

The recommendations made in this report were adopted, and appear to have met the requirements of the case, as the agitation now ceased.

In 1877, that is 10 years later, again a similar feeling arose in this Society, and again a large number of letters appeared on the subject in the *Chemical News*. Objection was taken to many of the candidates who obtained admission on account of their want of sufficient chemical training; at the same time those who objected not only had no plan for improving the working of the Society, but as far as our Society is concerned seem to have been convinced that it was practically impossible for the Chemical Society to insist on all its Fellows being trained and competent chemists, and, consequently, that another "organisation," as it was termed, among chemists was required, the object of which should be to ascertain whether a person had a chemical knowledge, and if so to stamp him as an efficient and competent chemist; in a word, this agitation led directly to the founding of the present Institute of Chemistry. The feeling at this time clearly was there must be two distinct Chemical Societies, one to which all who had any real interest in chemistry might belong, even if they had not had the advantage of a thorough training in chemistry, and the other a Society which should consist solely of trained and efficient chemists. The dissatisfaction which had manifested itself evidently arose from a feeling that in some cases Fellows were using the privileges of membership simply for commercial purposes, and that the new organisation would, to a great extent, obviate this; but still further to ensure the desired end the bye-laws were also altered, and a still more stringent declaration required from every one previous to his becoming a Fellow of the Society; and, further, an earnest attempt was made to develop the class of Associates. These were the results of this second agitation in our Society.

At the present time, after the lapse of 14 years, again a feeling somewhat of the same kind exists, at least among some of the Fellows, but the collateral circumstances are certainly distinctly different, for this organisation among chemists, the Institute, now exists, and all who desire to be stamped as thoroughly educated chemists have the opportunity of obtaining this recognition, which formerly was not the case. This does not, however, meet all objections, for it is not in any way a reason for allowing those, if such there be, who desire, but do not deserve, the milder title of F.C.S. to have it; and I am glad to say that the present Council have most carefully considered this matter, and have, in order that it should be carefully considered under every aspect, referred it to a special committee. The question is regarded by them as one of vital importance, but, like former Councils, they feel how much easier it is to cite objections to present arrangements than to suggest definite and workable plans for bringing about a state of things which would commend itself to all well-wishers to the Society. To make any satisfactory step in this matter, it seems to me absolutely necessary that we should first have a clear understanding as to whom we desire to attract to our Society, and whom to exclude from it. I am speaking, of course, entirely for myself, and I say I should wish to see the entrance easy to all who have any real interest in our science, even if they be only amateur chemists; I mean by that, all who are not in any way studying or following chemistry as a profession, but rather as a relaxation or relief it may be to ordinary business, as well as to those who are thoroughly trained and educated chemists; but in all cases with this single proviso, that socially there is no reason against their admittance into the Society. I give up entirely the idea that amount of chemical knowledge is to determine the suitability of a candidate; the title F.C.S. cannot be made a guarantee of chemical knowledge, we cannot gauge a candidate's ability and knowledge, and therefore desire to express no opinion concerning it, but we understand by his belonging to the Society that he has an interest in, and a desire to advance, chemical science. If, for commercial or tutorial or any other purpose, a man desires to proclaim to the world that he has a certain amount of chemical knowledge and experience, the Institute is obviously the Society to which he should belong, and more than that, if he does try to use the title F.C.S. for such a purpose, he is clearly doing what is not right.

The objects for which a scientific society exists are to stimulate the development of some branch of science by inducing intercourse among workers and students, and to disseminate new knowledge by publication. I do not, however, for a moment disguise from myself that difficulties and complications will arise even in carrying out so simple a definition as the foregoing one, and it is well openly and frankly to consider them. If chemistry was solely a science, I do not know that any of these complications would exist, but it is a profession, a business, as well as a science, and some believe that the F C.S. has in particular cases a certain money value, owing to the fact that at least a portion of the public still believe that a person who can write F.C.S. after his name must have valuable chemical knowledge. As the Institute grows and becomes more prominent, the misconception on this point will decrease, and it will be recognised as the body which gives this information, and that the Chemical Society does not give it and never pretended to do so.

At the same time a certain distinction does arise from the use of the title F.C.S., and if it be rightly understood it is natural and proper that it should be so; there may, therefore, be those who would be willing to pay the Society's annual subscription, for the honour and material advantage attendant on adding these letters to their name, and at the same time they may be people who have no interest in the science, never open any publication of the Society, and do not in the least care whether the science progresses or not. I believe their number is small, but few or many, these are the individuals which we should do our best to exclude from our Society; they are men who have got into the Society under false pretensions, and are not true to the obligations which they have signed. For the last 25 years successive Councils and many active and valued Fellows of the Society have been endeavouring to solve the problem of how to exclude such persons, and have not perfectly succeeded. I do not believe that it is to be done by hard and fast rules. I do not know of any great or radical change which would render the working of the Society even approximately perfect. I do not think that any such rules exist, and if we look back we find that the changes introduced from time to time to render the working of the Society more satisfactory have always been in the way of perfecting present laws rather than introducing new ones. In 1867, as I have pointed out, there was certainly a strong feeling that undesirable persons were becoming Fellows of the Society, and on the part of the Fellows strong measures were taken to call general attention to the fact, and how was this defect remedied? Not by any drastic or wide-sweeping alteration in the constitution of the Society, but simply by carrying out more fully the existing laws, throwing more of the responsibility of the elections on the Fellows themselves, and the only alteration of the bye-laws made was the increase of the number of signatures required to a schedule from three names to five. This was effective, and the Society went on increasing and developing more rapidly than before. Again, in 1877, the same kind of thing happened and was dealt with in the same kind of way: now the obligation was altered, and made more stringent, but no short cut could be found to a way for excluding undesirable members, although evidently it was felt, as before, that the line to be adopted was to raise and maintain among the Fellows a feeling that the Society was still a scientific Society, and that all its members should do their best to prevent those who would use it for unworthy purposes from becoming Fellows. Now, since this time, some 14 years, what has been the history of our Society, have those means been at all effective or not; has our Society advanced or receded? No one can doubt for a moment what the answer is. As far as numbers are concerned, in 1877 there were 916 Fellows; now there are 1752, nearly double as many, and as to the present position of the Society, without a shadow of doubt I say the Society never stood so high, both in the scientific and external world, as it does at the present moment. It has, like all scientific societies, gained its place in the community at large by the work it has done, and by the position which its Fellows have earned in science, and my experience during the last two years has proved to me how widely our Society is known, and in how favourable a light it is regarded, both at home and abroad. We hold a high position, and we have not only to maintain but to still further improve that position, and I do not for a moment believe that the Fellows of this Society will at any time tolerate the admission of members whose object is of a character to defile the Society. But the question how can the admission of undesirable persons be best prevented has still to be considered. I believe the surest way is following the course which former experience indicates; throw still more of the responsibility on the members, let them feel that it lies with them to keep up the character of their Society. I am glad that the Council have taken this view of the matter, and that the alterations which have of late been adopted by them are all steps in this direction. The obligation is to be more prominently insisted on; the Council proposing that it shall form a heading to every certificate, so that from the very first, the candidate shall know to what he is required to subscribe, and, consequently, that he shall have nothing to urge against the Council insisting at any time on his carrying out strictly and faithfully what he has undertaken. Another and, I think, a very important step taken lately by the Council is the publication in the Proceedings of the certificates sent in by candidates; the Fellows of the Society are thus put in possession of all the information which is supplied with regard to the candidate; they have the opportunity of carefully examining and considering it, and also have it for future reference. This leads me to a point which, I believe, is of considerable importance, and is again only an extension of what has been done on former occasions: it is the cultivation of a stronger feeling of responsibility in signing the certificate of any candidate. At one time it really was little more than a mere form; for then none but desirable persons wished to be Fellows of the Society; but at the present day, as we have seen, there may be inducements for unworthy people to seek admittance; consequently I do not see how any honourable man can conscientiously sign a certificate from personal knowledge without feeling in his own mind satisfied that the applicant is desirous of joining the Society from right motives and with proper intentions. I do not imagine that a man's motives can be gauged as surely as his height or his weight, but I do believe that if the feeling be cultivated and generally acknowledged that the body of Fellows expect and require that all should act thus honestly and honourably towards one another, then the undesirable persons who would be nominated for election as Fellows of our Society would be very few, so few that their influence would be absolutely inappreciable and their position so anomalous that they might be left to work out their own destruction. On learning that any Fellow is acting in any way dishonourably or wrongly towards the Society, it seems to me that the first feeling should be to ascertain who introduced the delinquent, who are the five Fellows who told us that he was a proper person to join our Society: and I am glad to think that now every member will be in a position easily to answer this question for himself; the date of the election will be given in the list of members, and in the Proceedings will be found the names of those who signed the certificate. Nothing is more powerful than public opinion; and if it is felt that this is the spirit in which elections are to be made, it will do far more good to the Society than any law which can be invented or enforced.

Again I would allude to the importance of a full agreement as to the real object of our Society and the class of candidates that we desire to welcome as brother members; this is the starting point for all concerted action, and I think there is now a much greater uniformity of opinion on this subject than there was formerly, for I believe few, if any, advocate looking on the title F.C.S. as even an approach to a scientific degree. But there is one other class of persons who use and consequently abuse the title F.C.S. to whom I have not alluded: it is those who have no right at all to it, who are not Fellows of the Society. Such cases are not rare, and this applies to other societies as well as to ours. To enable the Council to deal effectually with such cases, they took legal opinion on the matter, and found that practically they could not, with any hope of success, institute legal proceedings against this class of delinquents, and were advised that the only really efficient step to be taken in the matter was to promote a Bill in Parliament to render it penal for any one to use the initials attached to a Society to which he did not belong. In conjunction with other scientific societies, namely, the Royal Astronomical, Antiquarian, Geological, and Linnean, your Council have had a Bill for the above purpose drafted, and hope to be able very shortly to get it introduced into Parliament. For myself, I confess I have no fear for the future of our Society; it is certain to grow, both in strength and in usefulness, and that too along the right lines; temporary checks it may meet with, on studying its past history, it seems to me remarkable that the checks it has received have been so few and so insignificant. In common with, I believe, all similar societies, outbreaks of blackballing occur now and then: it is, perhaps, only a symptom of health and vigour, and relieves the Society from what might otherwise become a real danger. There is, however, a danger in such outbreaks, which is that they should arise from unworthy motives, and be carried on without discretion. Differences of opinion, fortunately, will always exist in a large Society like ours, and any Council worthy of directing such a Society will always be glad, nay desirous, of learning the views of the members, and the members should be desirous, and encouraged openly and frankly, to express their views with regard to the management and development of the Society.

I desire now, on resigning this Chair, most sincerely to thank the Fellows of the Society for the great honour which they conferred upon me in electing me their President, and allowing me to occupy a position which has been filled by so many distinguished chemists. I have endeavoured, as far as I was able, to perform efficiently the duties of the office—duties which I think it is a good sign are becoming every year more and more numerous. I cannot, however, conclude without saying a word of sincere thanks to the officers and Councils with whom I have had to work; it is on them the well-being of the Society mainly depends; and I feel how fortunate I have been, and how much my responsibilities have been lessened owing to the Society having the services of officers so able and so devoted to its interests as those are with whom I have been associated.

Dr. Gilbert proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed; the motion was seconded by Mr. Carteighe Both speakers referred in most appreciative terms to Dr. Russell's services to the Society, especially on the occasion of the Jubilee celebration. Dr. Teed supported the motion, which was carried by acclamation. The President having acknowledged the vote,

Professor Thorpe, the Treasurer, gave an account of the financial position of the Society. The receipts from Fellows had been £3459 16*s.* 0*d.*; from sale of the Journal £383 9*s.* 4*d.*; and by dividends on invested capital £363 0*s.* 6*d.* The expenses on account of the Journal had been £2724 0*s.* 10*d*; on account of the Library £300 18*s.* 9*d.*; on account of the Proceedings £183 7*s.* 10*d.*—the total expenditure being £3790 4*s.* 9*d.* The balance at the bank was £1798 17*s.* 7*d.*; and £600 had been invested in Metropolitan Board of Works 3½ per cent. stock.

Professor Attfield proposed that the thanks of the Fellows be tendered to the Treasurer. Dr. Atkinson, in seconding the vote, lamented the loss of income during the year, and referred to the smaller expenditure out of the Research Fund, and the excessive balance at the bank.

DR. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 20, 1890, TILL MARCH 19, 1891. CR.

	£	s.	d.	£	s.	d.
Balance at Bank March 20th, 1800	2,035	9	7			
,, in hands of Treasurer	0	13	0	2,036	2	7
Receipts by Life Compositions, Admission Fees, and Subscriptions from March 20th, 1890, to March 19th, 1891.						
15 Life Compositions at £20	300	0	0			
119 Admission Fees at £4	476	0	0			
2 Subscriptions for 1887 at £2	4	0	0			
23 ,, ,, 1888 at £2	47	0	0			
1 ,, ,, ,, at £1						
95 ,, ,, 1889 at £2	191	0	0			
1 ,, ,, ,, at £1						
365 ,, ,, 1890 at £2	738	16	0			
1 ,, on act. £1 16s.						
7 ,, ,, 1890 at £1						
836 ,, ,, 1891 at £2	1,697	0	0			
25 ,, ,, ,, at £1						
3 ,, ,, 1892 at £2	6	0	0	3,459	16	0
Sale of Journal and General Index. Journal, £382 19s. 4d; Index, 10s.				383	9	4
Subscriptions for Royal Society Proceedings				2	10	0
,, from Institute of Chemistry				6	5	0
,, from Society of Chemical Industry (2 years)				9	9	0
,, from Society of Public Analysts				4	4	0
Year's Dividends on Metropolitan Board of Works 3½ per cent. Stock: Three months on £6,130: Nine ,, on £6,730				224	11	0
Year's Dividends on £4,000 3 per cent. Consols				107	5	0
Year's Dividends on £788 London and North Western Railway Debenture Stock				30	14	6
Assets.						
Balance at Bank	1,798	17	7			
,, in hands of Treasurer	2	8	7			
3 per cent. Consols	4,000	0	0			
Metropolitan Board of Works 3½ per cent. Stock	6,730	0	0			
London and North Western Railway Debenture Stock	788	0	0			
	13,319	6	2	6,264	6	5

	£	s.	d.	£	s.	d.
Expenses on Account of the Journal.						
Salary of the Editor	300	0	0			
Salary of the Sub-Editor	150	0	0			
Miscellaneous Expenses of Editor	6	19	1			
Fees to Abstractors	336	18	9			
Printing of Journal	1,571	7	9			
Distribution of Journal	358	15	3	2,724	0	10
Expenses on Account of the Library.						
Salary of Librarian	50	0	0			
,, Library Attendant	62	0	0			
Books and Periodicals	96	10	0			
Binding	92	8	9	300	18	9
Printing Authors' Copies				46	10	3
Printing and Distribution of Abstracts of Proceedings				183	7	10
Miscellaneous Printing				80	1	8
Stationery				32	11	2
Inhabited House Duty and Income-tax				7	8	9
Repairs				18	6	5
Collector's Commission on Subscriptions				174	0	0
Treasurer's Stamps and Drafts, and Charges on Drafts				5	15	7
House Expenses.						
Providing Refreshments	19	2	10			
Lighting the Building (gas)	56	15	3			
Heating ,, (coals)	14	2	6			
Cleaning ,,	20	0	0			
Petty House Expenses	10	7	0			
House Porter's Wages	60	12	6			
Gate Porter and Watchman	2	2	0	183	2	1
Honorarium to Treasurer's Assistant				10	0	0
Treasurer's Petty Cash Disbursements				0	4	5
Expenses in connection with Anniversary Dinner, 1890				23	17	0
Purchase of £600 Metropolitan Board of Works 3½ per cent. Stock				672	15	6
Balance at Bank				1,798	17	7
,, in hands of Treasurer				2	8	7
				6,264	6	5

Audited, with vouchers, and found correct.
March 21st, 1891.

HOLLAND CROMPTON.
ROBERT H. DAVIES.
BERNARD DYER.

TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH RESEARCH FUND.

FROM MARCH 20TH, 1890, TILL MARCH 19TH, 1891.

Dr.

		£	s.	d.
1890.				
Mar. 20.	Balance at Bank	540	6	4
	Year's Dividends on £1,000 North British Railway 4 per cent. Stock	39	0	0
	Half year's Dividends on £4,000 Metropolitan Board of Works 3½ per cent. Stock	68	5	0
	Half year's Dividends on £4,400 Metropolitan Board of Works 3½ per cent. Stock	75	1	6
		£722	12	10

Cr.

	£	s.	d.
Grant to F. S. Kipping	15	0	0
„ Cross and Bevan	25	0	0
„ E. A. Werner	10	0	0
„ Linder and Picton	10	0	0
Purchase of £400 Metropolitan Board of Works 3½ per cent. Stock	445	10	6
Balance at Bank	217	2	4
	£722	12	10

Assets.

	£	s.	d.
Metropolitan Board of Works 3½ per cent. Stock	4,400	0	0
North British Railway 4 per cent. Stock	1,000	0	0
Balance at Bank	217	2	4
	£5,617	2	4

Audited, with vouchers, and
found correct,
March 21st, 1891.

HOLLAND CROMPTON.
ROBERT H. DAVIES.
BERNARD DYER.

Dr. Stevenson advocated a larger expenditure on the Library. Mr. Friswell followed Dr. Atkinson in lamenting the diminution in income and its cause, and also referred to the disproportion borne by the life composition fee to the annual subscription. Mr. Cassall asked that increased facilities of using the Library might be granted to Fellows.

The President said that every effort was made by the Library Committee to obtain books, and that if Dr. Stevenson and others who complained of deficiencies would point out what was required, the Library Committee would most certainly pay the utmost attention to their recommendations. The Library would be open at any reasonable and rational time.

[Dr. Thorne subsequently stated that the statistics of attendance on evenings other than those when meetings took place in the buildings were such as to indicate that there was no great desire to use the Library in the evenings.]

It so happened that a considerable sum had been voted out of the Research Fund at a time just outside the financial year, so that actually the expenditure was greater than appeared.

The Treasurer, in acknowledging the vote of thanks, said that the large balance would very soon disappear, as a number of heavy payments had to be made. He took occasion to gratefully acknowledge the service which Mr. Tutton had rendered him in keeping the Society's accounts, and finally proposed that thanks be given to the Auditors, Messrs. H. Crompton, R. H. Davies and B. Dyer. This proposal was seconded by Dr. Collie and adopted. Mr. Dyer having replied,

Professor Ramsay moved a vote of thanks to the Officers and Council, which was seconded by Mr. Friswell, and acknowledged by Dr. Armstrong.

Mr. Warington finally proposed that thanks be tendered to the Editor, Sub-Editor, Abstractors and Librarian. Dr. Clowes seconded the motion. Mr. Groves and Dr. Thorne replied.

Scrutators having been appointed, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session.

President: Dr. A. Crum Brown, F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, K.C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: G. Carey Foster, F.R.S.; W. N. Hartley, F.R.S.;

John Pattinson; J. Emerson Reynolds, M.D., F.R.S.; William A. Tilden, F.R.S.; Robert Warington, F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council: E. Atkinson, Ph.D.; Henry Bassett; Norman Collie, Ph.D.; John Ferguson, M.A.; E. Kinch; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; S. U. Pickering, M.A.; Boverton Redwood; Thomas Purdie, B.Sc.; John A. Voelcker, Ph.D.

The meeting then proceeded to consider the alterations in the bye-laws proposed by the Council. The first alteration having been read to the meeting,

Mr. Lloyd asked the President what would be his ruling with reference to any new proposal made at the meeting to alter the bye-laws.

The President said that he could not allow any proposal to alter the bye-laws of which notice had not previously been given to the Fellows to be put at that meeting. Although there was no express provision to that effect either in the charter or bye-laws, it was manifestly inexpedient to adopt any other course, and such ruling would be in accordance with the practice of the Society hitherto.

Mr. Lloyd stated that the movement in which he and others had taken part had for its object to exclude those who were personally objectionable, and to effect this they desired to place the nomination of Fellows in the hands of the Council. He therefore moved as an amendment that the whole subject of the alterations in bye-laws be postponed.

The President having ruled this amendment out of order, after a few remarks from other speakers, a vote was taken, and the following alteration in the bye-laws was carried, there being only five dissentients.

> "That in the case of candidates resident abroad unable to obtain the before-mentioned number [five] of signatures, the Council shall have power to accept a certificate, signed from personal knowledge by one Fellow of the Society, and to recommend its presentation for ballot."

Subsequently the following were also put to the meeting and carried all but unanimously.

2. That the following notice be printed at the head of the Form of Recommendation :—

"The attention of the candidate in whose favour this certificate is made out is specially directed to the fact that, if elected, he will be required to sign the following obligation prior to his admission into the Society:—

"Obligation.—I, the undersigned, do hereby engage that I will endeavour to promote the interests and welfare of the Chemical Society, that I will observe its laws, and to the utmost of my power maintain its dignity, as long as I shall continue a Fellow thereof.

3. That Bye-law XII be altered so that it read as follows:—

"An Annual General Meeting of the Society shall be held on the 30th day of March, or on some day in March near that time, and at such an hour as the Council may determine, for the election of Officers, &c."

John Pattinson; J. Emerson Reynolds, M.D., F.R.S.; William A. Tilden, F.R.S.; Robert Warington, F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council: E. Atkinson, Ph.D.; Henry Bassett; Norman Collie, Ph.D.; John Ferguson, M.A.; E. Kinch; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; S. U. Pickering, M.A.; Boverton Redwood; Thomas Purdie, B Sc; John A. Voelcker, Ph.D.

The meeting then proceeded to consider the alterations in the bye-laws proposed by the Council. The first alteration having been read to the meeting,

Mr. Lloyd asked the President what would be his ruling with reference to any new proposal made at the meeting to alter the bye-laws.

The President said that he could not allow any proposal to alter the bye-laws of which notice had not previously been given to the Fellows to be put at that meeting. Although there was no express provision to that effect either in the charter or bye laws, it was manifestly inexpedient to adopt any other course, and such ruling would be in accordance with the practice of the Society hitherto.

Mr. Lloyd stated that the movement in which he and others had taken part had for its object to exclude those who were personally objectionable, and to effect this they desired to place the nomination of Fellows in the hands of the Council. He therefore moved as an amendment that the whole subject of the alterations in bye-laws be postponed.

The President having ruled this amendment out of order, after a few remarks from other speakers, a vote was taken, and the following alteration in the bye-laws was carried, there being only five dissentients.

> "That in the case of candidates resident abroad unable to obtain the before-mentioned number [five] of signatures, the Council shall have power to accept a certificate, signed from personal knowledge by one Fellow of the Society, and to recommend its presentation for ballot."

Subsequently the following were also put to the meeting and carried all but unanimously.

2. That the following notice be printed at the head of the Form of Recommendation:—

"The attention of the candidate in whose favour this certificate is made out is specially directed to the fact that, if elected, he will be required to sign the following obligation prior to his admission into the Society:—

"Obligation.—I, the undersigned, do hereby engage that I will endeavour to promote the interests and welfare of the Chemical Society, that I will observe its laws, and to the utmost of my power maintain its dignity, as long as I shall continue a Fellow thereof."

3. That Bye-law XII be altered so that it read as follows:—

"An Annual General Meeting of the Society shall be held on the 30th day of March, or on some day in March near that time, and at such an hour as the Council may determine, for the election of Officers, &c."

OBITUARY NOTICES.

HENRY BOWMAN BRADY was born at Newcastle-upon-Tyne in 1835, and from his father, a surgeon in extensive practice, he inherited a taste for chemistry in its relations to medicine. He was apprenticed to a pharmaceutical chemist at Leeds, and subsequently carried on the business of a manufacturing and pharmaceutical chemist in Moseley Street, Newcastle, from 1855 to 1876. His habit of mind was thoroughly scientific, and he devoted himself with ardour to the development of pharmacy. He served for many years on the Council of the Pharmaceutical Society, and was one of the Examiners of that body. He was the originator of the Pharmaceutical Congress, and its President in 1872—73; and contributed numerous important papers to the *Pharmaceutical Journal.* He was elected a Fellow of the Chemical Society in 1859.

Besides being interested in the advancement of chemical knowledge, he had strong natural history tastes also. In his native city he lectured on botany, and contributed papers on marine fauna to local societies. On his retirement from active business life, he conducted extensive biological researches, becoming the chief authority in this country on recent and fossil Foraminifera. He published many original papers on recent forms of these lowly organisms, concluding with his great Monograph in the Reports of the "Challenger" Expedition 1873—76. This report, covering 814 quarto pages and illustrated by 115 plates, is the standard work of reference on the subject.

Dr. Brady belonged to the Society of Friends, and though he did not adopt the outward signs of that body, he retained the straightforwardness and kindliness so characteristic of its members. Of late years he suffered from ill-health, which travel in all parts of the world failed to alleviate. The severe weather of last winter told on his weak constitution, and he was carried off by inflammation of the lungs on January 10th of this year.

Dr. Brady was a Fellow of many Societies, both in England and abroad. He was elected into the Royal Society in 1874, and served as a member of its Council. In 1888 he received the honorary degree of LL.D. from the University of Aberdeen, and in the same year the Emperor of Austria presented him with the gold medal for Arts and Sciences, the highest order that a scientific man can receive in that Empire.

Cosmo Innes Burton was born in Edinburgh in the year 1862, his father being Dr. John Hill Burton, the well known Scottish historian, and his mother, a daughter of Cosmo Innes, Professor of History in the University of Edinburgh. His scientific tastes early displayed themselves, some of his happiest hours, as a boy, being those spent with his brother, now Professor of Sanitary Engineering at Tokio, in the little chemical laboratory which they had fitted up in the quaint old house in the outskirts of Edinburgh where the historian and his family lived.

He entered the University of Edinburgh in 1879, and during the following three years worked assiduously at Chemistry under the guidance of Professor Crum Brown, studying at the same time the various other subjects required for graduation in science. In 1881, on passing the first B.Sc. examination, he gained the Neill-Arnot Prize in Physics.

The next two years were devoted to the pursuit of chemical study at Munich with Professor Erlenmeyer, and at Paris with the late Professor Wurtz, where he also gained some experience in the method of original investigation. He assisted the late Professor Henniger in his researches on Erythrol and Professor Hanriot in his work on Strychnine.

After graduating B.Sc. in Edinburgh, in 1884, and gaining the Hope Prize in Chemistry, he became assistant to Professor Japp at South Kensington, in conjunction with whom he contributed four memoirs to the *Journal of the Chemical Society*, entitled, "Conversion of Ditolane-azotide into Diphenanthrylene-azotide," "On some Azines," "Anhydracetonebenzil," and "Condensation Compounds of

Benzil with Ketones." Organic research, however, had not much charm for Burton; his interests in chemistry were essentially of a practical nature. The intellectual inheritance he had received from his parents displayed itself in a philosophic, and at the same time practical, interest in the social problems of the day, and he desired some work in his profession which promised a quicker return of benefit to his fellow-men than the matters to which he had been devoting his energies at South Kensington. He, therefore, eagerly embraced the opportunity offered to him by the Town Council of Edinburgh of examining the air of public buildings in that city. He made a careful chemical and biological investigation of the air of the chief schools and theatres of the city, and drew up an exhaustive report on the subject, which was published in the minutes of the Town Council.

During the next two winters he acted as Lecture Assistant in Chemistry at the United College, University of St. Andrews, where he was well known to both professors and students. His interests being always aroused by his surroundings, whatever they might be, he devoted all his spare time to devising a direct method of estimating iodides in sea water. His figure, bent under the weight of a heavy keg of salt water, slung over his back, was a familiar sight in the early winter mornings on the pathway up the cliffs towards the college laboratory.

On leaving St. Andrews, he threw himself eagerly into an investigation of the heat produced by the compression of pure solid and liquid substances, for which the Royal Society had given him a grant of money, and Professor Tait the use of the necessary apparatus. The results of this research will be published by Mr. W. Marshall, F.C.S., who was associated with him in the work. His practical interests at the same time found expression in a course of lectures to working men, given by permission of Professor Crum Brown, in the University class-room, and in lecturing under the auspices of the University Extension Association. He also contributed a paper "On a Constant Daniell Cell for use as a Standard of Electromotive Force," and another in conjunction with Mr. A. P. Laurie, "On the Heat of Combination of Metals with Halogens" to the *Proceedings of the Royal Society of Edinburgh.*

Mr. Burton received the appointment last spring to the Professorship of Chemistry in the recently established Technical Institute of Shanghai. After being married, he proceeded with his young wife to Shanghai, where he arrived in July, and at once set about the duties of his post, which were exactly of the practical kind he had long sought, and which promised to give full scope to his remarkable powers. In the beginning of October he wrote, full of enthusiasm and hope, about his work; on the last day of that month he was cut down by an attack of malignant small-pox after two or three days' illness. The news of his death was received with feelings of the deepest regret by a wide circle of scientific friends in this country, who esteemed him as one of the most original of the younger generation of chemists, and predicted for him a distinguished career in his profession.

THOMAS CARNELLEY was a native of Manchester, in which city he was born on October 22nd, 1854. His father, Mr. William Carnelley, is the present chairman of directors of Messrs. Rylands & Co. Limited, with which firm he has for many years been connected.

His early education was received at King's College School, London, and during this period he attended the evening classes in chemistry at the College to which the school is attached, and in this way began the study of the science with which he in after life became identified. At the age of 16, he gained a Dalton Mathematical Exhibition at the Owens College, Manchester, in which institution he remained a student until 1872, retaining an official connection with it until the year 1879. Carnelley's studentship was one of exceptional brilliance, as shown by the record of successes gained at the Owens College, and also by the honours gained at the several examinations for the Bachelorship of Science of the London University, in which University he matriculated in the year 1870. At his first examination for the Bachelor of Science, in 1871, he was placed third in Third Class honours in Chemistry, and at the final examination, in 1872, obtained the degree, and was placed second in First Class honours in Chemistry, with marks qualifying for the University Scholarship in Chemistry.

Whilst preparing for those examinations, Carnelley also found time to devote himself to an investigation on the subject of the Vanadates of Thallium, a research for which, in 1872, the Dalton Chemical Scholarship was awarded to him; and in consideration of his success at the final B.Sc. examination, the holding of the Scholarship was extended to a third year.

During the years 1872–74, Carnelley acted as private assistant to Professor Roscoe, and began his career as a teacher by giving lectures in connection with the evening classes at the Owens College. The next year he spent in Germany, devoting himself to the study of chemistry at the University of Bonn, under Professors Kekulé, Zincke, and Wallach, being engaged during a portion of this period with the investigation of the "Effect of Passing the Mixed Vapours of Carbon Bisulphide and Alcohol over Red-hot Copper," also with the preparation and properties of the hydrocarbon "Tolylphenyl."

In the year 1876, Carnelley obtained the degree of Doctor in Science in Chemistry, in the University of London; and from the year 1875 to 1879 he held the appointment of Assistant Lecturer and Demonstrator in Chemistry at the Owens College; during a portion of this period he also discharged the duties of Principal of the North Staffordshire School of Science, at Hanley, to which institution he rendered great services by his teaching and powers of organisation.

In 1879, the Firth College at Sheffield was founded, and Dr. Carnelley was appointed to the Chair of Chemistry. The three years he remained in Sheffield were actively occupied with the fitting up of the chemical laboratory, organising the teaching in his department, and the pioneer work which is always required at the hands of the teachers in such newly founded institutions.

From Sheffield, Carnelley, in 1882, passed to Dundee to take up the duties of the first Professor of Chemistry in the then recently established University College. Here ample means for the building and equipment of the department were placed at his disposal, and he had the satisfaction of superintending the erection of the block of buildings in which are located the chemical laboratories, lecture rooms, &c., arranged in accordance with his own plans and ideas.

The College at Dundee is in no small degree indebted to its first Professor of Chemistry for the success which it has achieved in the few years since its foundation. His zeal and untiring energy, his unselfish devotion to his work, contributed to make the Chemical Department one of the most important in the new College. Carnelley's first care was naturally the establishment of a School of Chemistry, in which the subject should be taught in a truly scientific spirit, but from one who had received his education in a large industrial centre, such as Manchester, the practical application of the science would naturally receive some attention, and we find him busied with the establishment of a Dye-house and Technical Museum, which were designed to be an off-shoot of the Chemical Department. These were not, however, completed before he had ceased to be Professor at Dundee, but although he had in 1888 been appointed to the Chair of Chemistry in the University of Aberdeen, he had the satisfaction of being present at the opening of the new Dye-house and Technical Museum, the materials for the latter having been presented by Professor Carnelley and his father to the College in the early part of 1888. On this occasion, he delivered an inaugural lecture, in which he clearly set forth his views and ideals as a teacher of Chemistry. "Let Chemistry be taught in a truly scientific spirit for the real love of it, and its practical applications will follow and indeed accompany it, as certainly as the phenomena of daylight follow the rising of the sun. In no country has Chemistry been taught in a more scientific spirit than in Germany, and it is there that some of its most important practical applications have been made" Such words have a special force, coming as they did from one who had all his life worked in busy industrial centres, and who had shown himself ready and able to care for the advancement of applied science, and it is well that the truth contained in these words should in these days be specially held in remembrance, when we hear so much of "technical education" and so little of "scientific education;" for our industries can alone receive the benefit of scientific knowledge and scientific training when these are given in the broadest and the most liberal spirit.

Fortunate as the College in Dundee was in having secured as its Professor of Chemistry one who, as Carnelley showed himself to be, was well able to create an enthusiasm for his subject, he conferred lasting benefits on the town and its inhabitants by the investigations, chemical and bacteriological, of the air of dwellings and schools, which were carried out by him in Dundee. Such was the interest created by these investigations that he was elected a member of the School Board, and received a special commission from that body to prepare a Report on the Cost and Efficiency of the various systems of Heating and Ventilating Schools. The report was published in 1889, and deals in a very thorough and exhaustive manner with this all important but woefully neglected subject.

With the preparation of a treatise on the subject of "Air and Ventilation," he was busily engaged at the time of his last illness, and arrangements have been made for the completion and publication of this work.

This cursory glance at Carnelley's work during his six years' residence in Dundee enables one readily to understand that his acceptance of the Professorship in the University of Aberdeen should have been received with universal regret by his colleagues and fellow-townsmen.

He had not been settled two years in Aberdeen when he succumbed to a severe and sudden illness, caused by the formation of an internal abscess. He died at his residence, The Cults, Aberdeen, on August 27, 1890, at the comparatively early age of 36.

Actively engaged as Carnelley was in teaching from the year 1875 until the time of his death, still he found opportunities to contribute by numerous investigations to the advancement of his science. The last of his published papers show him to have been active in many branches, both of a purely scientific and of a practical character. Undoubtedly the work with which his name will ever remain identified is that undertaken with the object of extending Mendeléeff's

"Periodic Law." In the obituary notice published in *Nature*, September 25, 1890, it is stated that—

"Carnelley, when a student at the Owens College, appears to have been greatly impressed with Mendeléeff's conceptions, and it was to the study of the physical properties of the elements and their compounds, and to the devising of new methods of obtaining trustworthy determinations of the melting points of metallic salts and the elements, that he early devoted his energies. The results of these experiments were subsequently utilised to show that the fusibility of the elements and of certain of their compounds is a periodic function of their atomic weights. From the relationships discovered by him to exist between the melting points of the chlorides of the elements and the atomic weights of those elements, Carnelley was led to draw conclusions respecting the atomic weight of the element beryllium and to fix its position in the classification of the elements.

"Other physical properties have been shown by Carnelley to be related to the atomic weights of the elements, and in a paper read at the Aberdeen meeting of the British Association he developed a series of analogies between the elements and various series of hydrocarbons, from which he concluded that the chemical elements may be represented by a formula $A_nB_{2n+(2-x)}$, in which n is series and x the group to which the element belongs; $A = 12$ and $B = -2$. In a paper published in the *Philosophical Magazine* in January last, he tells us that since 1872 he had attempted to give the periodic law a simple numerical expression, and states that early in the summer of 1889 he had obtained such an expression, in which the atomic weight is represented as equivalent to the product of a constant, c, into a factor made up of m, a member of an arithmetical progression, dependent on the series to which the element belongs, and v, the maximum valency, or the number of the group of which the element is a member. Thus—

$$\text{“}A = c\,(m + v^{\frac{1}{x}}).$$

"The best results are obtained when $x = 2$, and m is 0 for series II., 2½ for III., 5 for IV., 8½ for V., 12 for VI., 15½ for VII., 19 for IX., 22½ for X., 26 for XI., and 29½ for XII.

"The formula thus becomes $A = c\,(m + \sqrt{v})$, and m is a member of an arithmetical series in which the difference is 3½, save in the first two series, when it is 2½. By using this equation, the value for c in the case of 55 elements is found to lie between 6·0 and 7·2, with a mean value of 6·64. Accepting 6·6 as the value of c, the calculated atomic weight of sodium, for example, would be found as follows:—Sodium is the first member of series III., m is therefore 2·5 and $v = 1$, so that $A = 6{\cdot}6(2{\cdot}5 + \sqrt{1}) = 23{\cdot}1$. In the paper referred to, the atomic weights of all the elements are given as calculated by this formula, and compared with those generally accepted. The results obtained exhibit very close approximation, the calculated values being, in fact, nearer the experimental numbers than those obtained by the aid of Dulong and Petit's law. The remarkable coincidence that the value 6·6 for the constant c in the above formula very nearly approximates to the value 6·4, accepted as the atomic heat of the elements, in accordance with Dulong and Petit's law, is noted, and that the specific heats of the elements may consequently be represented as equivalent to $\frac{1}{m + \sqrt{v}}$. The specific heats calculated by the aid of this formula are compared with the experimental values, and, in the case of the 55 elements in which a comparison can be instituted, in 45 instances the agreement is very satisfactory, while the other 10 are elements the specific heats of which, according to Dulong and Petit's law, are more or less abnormal.

"Accepting Bettone's conclusion that the hardness of an element is inversely proportional to its specific volume, it is shown that hardness may be represented in terms of the specific gravity, and the expression $6{\cdot}6(m + \sqrt{v})$, thus—

$$\text{“Hardness} = \frac{1}{\text{spec. vol.}} = \frac{\text{sp. gr.}}{\text{at. wt.}} = \frac{\text{sp. gr.}}{6{\cdot}6(m + \sqrt{v})}.\text{”}$$

Of the value and importance of Professor Carnelley's labours in this field, no one could well be found to speak with greater authority than Mendeléeff himself, who, in a letter addressed to Sir Henry Roscoe, dated February 5, 1890, wrote as follows.—

"Although Professor Carnelley's services to science are well known to you, I think it my duty to inform you that the name of Professor Carnelley is deservedly and widely known in every country which interests itself in investigations of the theoretical side of chemical science and especially with reference to the study of the chemical elements. The labours of Professor Carnelley connected with the periodic law of the elements have been so remarkable that the history of the subject would be incomplete if his name were omitted.

"The connection between the composition of metallic salts and the temperature of their melting points has been determined by the numerous and accurate researches of Carnelley, which have laid bare the internal meaning of this province of empiricism."

Carnelley was elected Fellow of this Society on February 19, 1874, and was the author of the following papers which have appeared in the Transactions of the Journal:—

(1.) Vanadates of Thallium. Trans., 1873.

(2.) Effect of Passing Mixed Vapours of Carbon Bisulphide and Alcohol over Red-hot Copper. Trans., 1875.

(3.) Tolylphenyl, a New Hydrocarbon. Trans, 1876.

(4.) High Melting Points, with Special Reference to Metallic Salts. Trans., 1876.

(5) Action of Water and of Various Saline Solutions on Copper. Trans., 1876.

(6.) High Melting Points. Part II. Trans., 1877

(7.) A True Method for Determining High Melting Points. Trans., 1877.

(8.) Influence of Ammonium Sulphide in Preventing the Action of Various Solutions on Copper. Trans., 1877.

(9) Oxidation of Ditolyl. Trans., 1877.

(10.) Tetrabromide of Tin (in conjunction with Mr. L. T. O'Shea). Trans., 1878.

(11.) Determination of High Melting Points. Trans., 1878.

(12.) Determination of High Boiling Points (in conjunction with Mr. W. Carleton Williams). Trans., 1878.

(13.) Boiling Points of Certain Metals and Metallic Salts (in conjunction with Mr. W. Carleton Williams) Trans., 1879.

(14.) The Melting and Boiling Points of Certain Inorganic Substances (in conjunction with Mr. W. Carleton Williams). Trans., 1880.

(15.) Action of Heat on the Mixed Vapours of Benzene and Toluene: two New Methylenediphenylenes. Trans., 1880.

(16.) Action of Heat on Mercuric Chloride under Low Pressure. Trans., 1882.

(17.) A New Form of Pyrometer. Trans., 1884.

(18.) Melting Point of Certain Inorganic Substances (in conjunction with Mr. L. T. O'Shea). Trans., 1884.

(19.) Brominated Derivatives of Diphenyl, Tolylbenzene, and Ditolyl (in conjunction with Mr. A Thomson). Trans., 1885.

(20.) Amidodiphenylsulphonic Acid and Azo-dyes from Diphenyl (in conjunction with Mr. J. Schleselman). Trans., 1886.

(21.) Derivatives of Tolylbenzene (in conjunction with Dr. Thomson). Trans., 1887.

(22.) The Dehydration of the Metallic Oxides by Heat, with Special Reference to the Polymerisation of the Oxides (in conjunction with Dr. J. Walker). Trans., 1888.

(23.) Solubility of Isomeric Organic Compounds and of Mixtures of Sodium and Potassium Nitrate, and the Relation of Solubility to Fusibility (in conjunction with Dr. Thomson). Trans., 1888.

(24.) The Antiseptic Properties of Isomeric Organic Compounds in Relation to their Constitution (in conjunction with Mr. W. Frew). Trans., 1890.

He also contributed several Notes which have been published in the Proceedings of this Society. In addition to the above contributions, he was the author of several papers which have appeared in the *Philosophical Transactions* and the *Proceedings of the Royal Society*, and was a contributor to the *Philosophical Magazine*, *Nature*, the *Chemical News*, the *Chemiker Zeitung*, and also to the "*Berichte*."

For many years Carnelley was on the staff of Abstractors for the Journal of this Society, and was the author of an elaborate and most valuable compilation of the boiling and melting points of chemical compounds, published in two large volumes—"a monument of industry and devotion to science." Carnelley also assisted in the editing of the *German-English Dictionary of Scientific and Technical Terms*, published by Messrs. Vieweg and Son.

Professor Carnelley's retiring, modest, unselfish, and deeply religious nature, his earnest enthusiasm, served not only to create in all a sincere regard for him, but to make him beloved by those who were privileged to become intimately acquainted with him. By his early death an already brilliant career has been deplorably cut short, and a vacancy created in the ranks of scientific men in this country which must long remain unfilled.

WILLIAM LANT CARPENTER, B.A., B.Sc. Lond., was the eldest son of the late Dr. W. B. Carpenter, C.B., F.R.S. He was born in the year 1841 at Bristol, but was educated in University College School, London, and studied chemistry under Professor Williamson in University College, London, and also in the Birkbeck Laboratory, taking the degrees of B.A. and B.Sc. in the University of London. He was, in 1859, engaged in the Broad Plain Soap Works, the proprietors of which were Messrs. C. Thomas Brothers, where, for nearly 20 years, he was a partner of the firm. At the termination of this partnership in 1881, Mr. Carpenter removed to London, and in 1882 he became connected with the School of Electrical Engineering in Hanover Square. Being engaged as Lecturer by the Gilchrist Trustees, he undertook the duties of this post, and threw into the work all the energy of an earnest and strong nature. For many sessions Mr. Lant Carpenter greatly distinguished himself as a most effective lecturer under the Gilchrist Trust, especially in the North of England and in Scotland. At Bristol he was engaged in philanthropic work under the auspices of Miss Mary Carpenter, his aunt, and during the greater part of his residence in Bristol he took a pronounced part as its Secretary in the management of the Boys'

Industrial School there. He frequently lectured at the Philosophical Institution in Bristol, was an active member of the Naturalists' Society, and much interested in the foundation of the University College, Bristol, on the Council of which he represented the University of London.

Thus he was led to take an interest in the education question generally, and of late years the working of the Education Acts and the importance of continuation schools and recreative evening classes engaged much of his attention. He was local secretary at the Bristol (1875) meeting of the British Association, and may truly be said to have taken a leading part in all movements for the promotion of science, and especially physical science, in the West of England, where he was well known as a lecturer on such subjects. He was in charge of the chemical and part of the physical investigations of the deep-sea explorations of H.M.S. "Porcupine" of 1869 and 1870, his report on which was printed in the *Proceedings of the Royal Society*. In 1881 he left Bristol, and settled at Harlesden, near London, in the following year.

William Lant Carpenter, besides being a member of the Institution of Electrical Engineers, was a Fellow of the Chemical Society, of the Society of Chemical Industry, and of the Physical Society. During the last ten years of continuous work his health had suffered a severe strain, and a holiday became necessary. This was taken in 1889, but, combined with a journey to look after the schools on the Indian reserves in the Dominion of Canada for the New England Company, the journey became a strain instead of a rest, very few nights of his absence from home not being occupied in travel, so as to economise time. His health broke down again early in 1890, and so a voyage was undertaken to Australia and New Zealand, which he had visited in 1880 in order to seek restoration from the results of a similar collapse. Unfortunately no good effects followed from this voyage, though subsequently at Shanklin and Bournemouth some improvement was apparent, and his friends began to entertain hopes of his ultimate recovery. These were, however, doomed never to be fulfilled, and he died on December 23, 1890, leaving his four children, his brothers, and a wide circle of friends to mourn his loss. He was a Liberal in politics and a Unitarian in religion, although he did not go to a Unitarian place of worship, but, like many of his co-religionists, attended the Presbyterian Church. He took a warm interest in Mrs. Humphry Ward's University Hall scheme.

With regard to Mr. Carpenter's publications, his excellent little book, compiled from his Gilchrist Lectures, entitled *Energy in Nature*, cannot be forgotten or overlooked, but since the once well-known, if not classic, work on the manufacture of soap by Morfit, no treatise on the chemistry and manufacture of soap has appeared which can be considered equal to Carpenter's work entitled *Soap, Candles, Lubricants, and Glycerin*, published by E. F. and N. Spon in 1885. Mr. Carpenter has also acted as examiner in the subject of soap manufacture for several years for the City and Guilds of London Institute. So solicitous was he not only for the condensation of the abstracts of English patents on the subject of fats, oils, and soaps appearing in the *Journal of the Society of Chemical Industry*, but that in such condensation adequate information should be given, that for several years, in addition to the heavy load of duty he had already taken on his shoulders, he undertook the abstracting himself of all patents bearing upon his favourite subject. In this earnest devotion to the part he had voluntarily undertaken to play both as member of Publication Committee and as abstractor, he thus followed closely in the steps of his distinguished and singularly devoted predecessor, Mr. Walter Weldon.

JOHN B. HUTCHESON, F.I.C., was born at Dunoon, Argyllshire, on April 10th, 1848, and was educated at the local Parish School. Early in 1867 he entered the laboratory of the late Professor Thomas Anderson, at Glasgow University, and after his student career, became one of Professor Anderson's private assistants. He left in 1869 to take the post of chemist to Messrs. Inglis and Wakefield, calico-printers and Turkey-red dyers, near Glasgow, where he remained for two years; in 1871, he returned to the University again as assistant to Professor Anderson; and when Professor Ferguson succeeded to the Chair of Chemistry, in 1874, Mr. Hutcheson was appointed one of the two official assistants. In this post he continued until his death, on April 15th, 1890. Mr. Hutcheson was married, and is survived by his wife, and a family of three boys and one girl.

Mr. Hutcheson, in 1882, devised a process for electrical bleaching, in conjunction with his colleague, Dr. Dobbie, now Professor of Chemistry at Bangor, an account of which was published in the Transactions of the Chemical Society of that year. He also, along with Dr. Dobbie, devised an easy method of taking the specific gravity of solids, which is described in the *Proceedings of the Philosophical Society of Glasgow* for 1884.

Mr. Hutcheson was a very successful teacher, both in his official capacity, and in his numerous private classes, and his duties absorbed most of his time. He was a thoroughly good and successful analyst, and had a large acquaintance with analytical processes.

His kind and courteous manners and his integrity of character made him a favourite with all the students whom he taught; and his early death was deeply regretted by all those who were his colleagues in the laboratory of Glasgow, as well as by his numerous other friends.

EDWARD CHAMBERS NICHOLSON, whose greatest achievements were coincident with the earlier stages of progress of the coal-tar colour industry, was born in January, 1827, at Lincoln, being the seventh son of the late Robert Nicholson, of Lincoln and Maidenhead. Owing to the death of his mother in the following year, he was, during boyhood, placed under the care of his aunt, Miss Chambers, of South Carlton, Lincolnshire, and when ten years of age was sent to Dr. Beesley's school, at Uxbridge. After completing his education there, he was placed for a time with a chemist and druggist at Andover, from whence he was transferred to the laboratory of Mr. Lloyd Bullock, in Conduit Street, London.

In October, 1845, young Nicholson entered as one of the first students the newly opened laboratories of the Royal College of Chemistry, under Dr. A. W. Hofmann, having for contemporaries, Messrs. Abel, Bloxam, De la Rue, Galloway, Rowney, and George Simpson. He was soon promoted to be an assistant, and helped the Professor in some of his earliest researches. Later, in 1848, he published, conjointly with his friend, F. A. Abel, an elaborate memoir on Strychnine and its Salts, by which the true constitution of this organic base was satisfactorily determined. This gained for the authors their election as Fellows of this Society.

Mr. Nicholson remained at the College until 1850, when he accepted an engagement offered him by Messrs. Fothergill and Co., of Aberdare, to investigate the chemistry of iron making. Here he made numerous experiments, conjointly with Dr. David Price, on the products of the hot and cold blast and refinery furnaces, but was forced to give up by a bad attack of typhoid fever, which induced his return to London. Then, shortly afterwards, in 1853, when sufficiently recovered, he joined his friends Messrs. Simpson and Maule, of Kennington Road, and helped to start the chemical factory at Locksfields, Walworth. Here he introduced improvements in the manufacture of pyrogallol, ether, collodion, &c., and the firm afterwards turned their attention to aniline and the coal-tar colours, which necessitated the building of a larger factory at Hackney Wick. During this period, Mr. Nicholson discovered the arsenic acid process of manufacturing magenta, but found himself anticipated by eight days by Dr. Henry Medlock's patent, of January 18th, 1860, which his firm afterwards purchased. The three large crowns of crystallised rosaniline acetate, shown in the International Exhibition of 1862, excited universal admiration; but the discovery of chrysaniline yellow, of the lower phenylated products of rosaniline, Alexandra violet, regina, &c., and the mode of rendering soluble the spirit dye known as Girard's blue, by a process of sulphonation in two stages, giving either the pure soluble blue for silk, or Nicholson blue, for wool, were amongst the greatest technical achievements. In August, 1868, Mr. Nicholson finally retired from his active chemical labours, but took a continued interest in the progress of scientific discovery. He was an original member of the Society of Chemical Industry, and a Fellow of the Institute of Chemistry. On the 23rd October last he died of cancer, in the sixty-fourth year of his age, leaving his widow and a numerous circle of friends to mourn his loss.

Henry Smith, M.D., Lond., Barrister-at-law, F.I.C.—We have to record the death of Dr. Henry Smith, at Paris, on Friday, the 20th June, 1890. He was born at Plumstead, in Kent, on the 15th November, 1857, and was therefore in his 33rd year. He was educated at the City of London School, and, having decided to study medicine, entered at St. Bartholomew's Hospital, where, after obtaining the Wix and Bentley Prizes, he became L.S.A. in 1879, a M.R.C.S. in 1881, and in the same year took the M.B. degree of the University of London, and in 1885 the M.D. degree from the same University. During these years he filled some of the most important resident medical appointments in London, being successively House Physician to the Hospital for Consumption, &c., Brompton, House Physician to St. Bartholomew's Hospital, House Surgeon, and subsequently House Physician, to the Hospital for Sick Children, Great Ormond Street. During his residence at the latter hospital, the first symptoms of the disease manifested themselves from which he ultimately died, and it is a matter of great regret to all that he did not at once take a long voyage; but his services had been so eminently successful in the afore-mentioned offices, and so warmly appreciated by all with whom he had been brought in contact, that he was reluctant to leave London, and forego the advantages he had gained.

His attention was now specially directed to public health questions; He took the Diploma in Public Health from the University of Cambridge, and was elected a Fellow of the Institute of Chemistry. He was appointed Public Analyst for Woolwich and for Plumstead, and Deputy Medical Officer of Health for the latter place.

In 1887, he was called to the Bar at Lincoln's Inn.

Unfortunately the dread disease, consumption, from which he suffered, slowly, but surely, made headway, and in 1888 he had to seek a more congenial atmosphere than that found in London; he accordingly went to Hastings, and in January, 1890, to Hyéres; he was on his way home when he died in Paris, only reaching that city on the morning of his death.

Dr. Henry Smith was a man of much common sense, of keen perception and great ability, kind hearted and sympathetic, greatly beloved and greatly regretted by all who knew him, and who had every reason to believe his career would have been eminently successful.

His remains were brought to England, and buried at the New Plumstead Cemetery on Friday, the 27th June, 1890, his burial being the first in the cemetery which his father, as Chairman of the Burial Board, had done so much to promote.

HEINRICH WILL was born at Weinheim, in Baden, on December 8th, 1812. After having passed through the Latin school of his native town, he took to pharmacy as a vocation, and in 1835 became assistant to Professor Geiger, in Heidelberg. After the death of the latter, he occupied a similar position with Leopold Gmelin. Leaving Heidelberg, he accepted an invitation of Liebig to come to Giessen, where he first filled the place of private assistant, receiving his doctorate in 1839. Shortly afterwards he assumed the directorship of the branch laboratory founded by Liebig. In 1844, he established himself as "Privatdocent," in Giessen. The following year he received an invitation to London, to establish a laboratory there, but this was refused on account of the success attending his labours at Giessen. A. W. Hofmann was afterwards invited, and accepted the appointment in London, in his place. In 1845 Will was appointed Extraordinary Professor.

Liebig, having been summoned to Munich, left Giessen in 1852, when Will and Kopp, who were made ordinary Professors in 1853, undertook the management of the chemical instruction, Will as director of the laboratory, and Kopp as teacher of chemical theory, until he went to Heidelberg in 1883. Will acted also as lecturer and teacher in the Giessen University till 1882, when he resigned. On May 1st, 1889, in conjunction with a large number of his pupils and friends, Will celebrated the fiftieth anniversary of his doctorship. In 1890 he was present at the unveiling of the Liebig monument, having acted as President of the Giessen Committee. On October 15th of the same year, he expired suddenly from apoplexy, without having shown any symptoms of previous illness.

Of Will's literary works may be mentioned:—

His *Anleitung zur chemischen Analyse*, a book which reached its 12th edition in 1883, and which is translated into almost all European languages. His activity in connection with the editing of *Liebig's Annalen* is well known. From the year 1656, he undertook the editing of the "*Jahresbericht ueber die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.*" This work was carried on conjointly with Kopp till 1862, and then by himself till 1868. Of his chemical work may be mentioned the following papers:—

1. "Contribution to the Theory of Organic Compounds," *Ann.*, **91**, 257.
2. "On the Composition of Chelidonine and Jervine," *ibid.*, **35**, 113.
3. "Researches on the Constituents of Vegetables" (in conjunction with Fresenius), *ibid.*, **50**, 363.
4. "New Methods for Determining the Value of Potash and Soda, of Acids, and of Manganese," *ibid.*, **47**, 89; and **49**, 125.
5. "A Number of Mineral Analyses" (partly in conjunction with Fresenius), *ibid.*, **45**, 431; **47**, 198; **52**, 66; **61**, 181; **81**, 23.
6. "Method for the Determination of Nitrogen in Organic Compounds (in conjunction with F. Varrentrapp), *ibid.*, **39**, 257; **45**, 95; and **48**, 147.
7. "On the Ether of Veratric Acid," *ibid.*, **37**, 198.
8. "Composition of the Ethereal Oil of Rue," *ibid.*, **35**, 235.
9. "The Action of Iodine on Aniseed and Fennel Oils," *ibid.*, **65**, 230.
10. "On Styphnic Acid" (in conjunction with R. Böttger), *ibid.*, **58**, 268.
11. "On Croconic and Rhodizonic Acids," *ibid.*, **118**, 177.
12. "The Composition of Lithofellic Acid" (in conjunction with C. Ettling), *ibid.*, **39**, 242.
13. "On Sulphate of Iron and Quinine," *ibid.*, **42**, 111.
14. "A Compound of Nicotine with Benzoyl Chloride," *ibid.*, **118**, 205.
15. "Research on the Constitution of the Essential Oil of Black Mustard," *ibid.*, **52**, 1.
16. "Contribution to the Knowledge of the Formation of Mustard Oil from the Seed of Black Mustard" (in conjunction with W. Körner), *ibid.*, **125**, 257.
17. "Investigation of Some Sulphuretted Compounds of Mustard Oil," *ibid.*, **92**, 59.
18. "A New Constituent of White Mustard Seed," *Wien. Akad. Ber.*, **61**, 3 Abh., 178.
19. "The Glucoside of White Mustard Seed," *Lieb. Ann.*, **199**, 150.

XLVI.—*The Addition of the Elements of Alcohol to the Ethereal Salts of Unsaturated Acids.*

By T Purdie, Ph.D., B.Sc, Professor of Chemistry in the United College, University of St. Andrews; and W. Marshall, B.Sc.

In former communications to this Journal, we have shown that, when a mixture of an ethereal salt and an alcohol is treated with a minute quantity of sodium alkylate, an extensive interchange of alkyl radicle takes place between the ethereal salt and the alcohol, and that this change is probably effected by the agency of an unstable intermediary compound, the alkyl derivative of an acid hydrol, formed by the addition of the elements of 1 mol. of the alcohol to 1 mol. of the ethereal salt.

We have also shown that in the case of the ethereal salts of fumaric and maleïc acids, this reaction is quickly followed by another, in which the elements of a molecule of alcohol are permanently added to the ethereal salt, an alkyloxy-derivative of succinic ether being produced. Various isolated instances of a similar addition of alcohol to unsaturated ethereal salts have been recorded: thus, ethylic benzalmalonate, on saponification with alcoholic potash, yields potassium ethoxybenzylmalonate, and by the action of sodium ethylate and ethyl alcohol on pyrocitric ethers, ethoxypropanedicarboxylic ethers are obtained.

The various changes undergone by ethereal salts under the action of sodium alkylates is a subject of considerable interest, such reactions having been so frequently employed in recent investigations; it seemed to us, therefore, worth while to ascertain if the ethereal salts of unsaturated acids in general can be converted into saturated compounds by union with the elements of alcohol through the agency of small quantities of sodium alkylates.

We find that the ethereal salts of acrylic and crotonic acids very readily enter into permanent combination with the elements of alcohol, but that those of various other unsaturated acids are incapable under the conditions of our experiments of undergoing the change alluded to.

Ethereal Salts of Fumaric and Maleïc Acids.

Methylic Methoxysuccinate.—In our previous experiments with the ethereal salts of fumaric and maleïc acids (Trans, 1881, **39**, 344; 1885, **47**, 855), we did not succeed in isolating in the pure state the ethereal salts of the alkyloxysuccinic acids which we assumed to be formed from them by the addition of alcohol. We now find that methylic methoxysuccinate may be readily obtained by treating methylic fumarate in the cold with anhydrous methyl alcohol and minute quantities of sodium methylate.

The methylic fumarate is most easily prepared by heating a mixture of the acid with twice its weight of anhydrous methyl alcohol, and one-fifth its weight of strong sulphuric acid on the water-bath, using a reflux condenser. On cooling, the ethereal salt crystallises. The contents of the flask are shaken with a solution of sodium carbonate; the crystals are collected, pressed, dried over sulphuric acid, and distilled. After one distillation, the substance boils at an almost constant temperature, and is about equal in weight to the acid used.

Methylic fumarate is only slightly soluble in cold methyl alcohol; when, however, it is treated with an equal weight of this alcohol, in which sodium has been dissolved in the proportion of $\frac{1}{25}$th of an atom to 1 mol. of the fumarate, it begins at once to go into solution, and after 48 hours, is entirely dissolved. The mixture is poured into water and shaken with ether. The ethereal extract, after evaporation, leaves a syrup which, on standing, solidifies to a hard, crystalline mass consisting of nearly pure methylic methoxysuccinate. 50 grams of methylic fumarate yielded by this method 51 grams of dry, crystalline residue, which, after hydrolysis with sodium hydrate and acidifying strongly with nitric acid, gave no precipitate of fumaric acid. It appears, therefore, that the reaction is very complete.

Methylic methoxysuccinate melts at 28°, boils at 218—220°, and dissolves readily in alcohol, ether, benzene, chloroform, and carbon bisulphide, and also, though sparingly, in cold water. The substance crystallises beautifully; from its solution in carbon bisulphide or water, it may be procured in very large, highly refracting and perfectly developed crystals resembling the monoclinic forms of gypsum. The results of the analysis of the substance are given below.

In a previous communication (*loc. cit.*), we have adduced evidence to show that the ethereal salts of fumaric and maleïc acids yield those of the same alkyloxysuccinic acids by the addition of the elements of alcohol. Certain slight differences, however, were observed in the properties of the zinc methoxysuccinates obtained from the two sources, and it was left in doubt whether these differences were due to impurities in the substances, or possibly to isomerism. In order to decide this point, the crystallised pure zinc salts being obtainable with difficulty, we prepared methylic methoxysuccinate from methylic maleate. The method of preparation was essentially the same as that adopted in the case of methylic fumarate, and the reaction was found to proceed in the same manner. 20 grams of methylic maleate yielded 18 grams of dry methylic methoxysuccinate, which, in its mode of crystallisation and melting point, was identical with the substance obtained from methylic fumarate. Fumaric and maleïc acids, therefore, yield the same saturated acid by combination with the elements of alcohol, a result which is in entire accordance with the known relations of the two acids.

The methylic salt of methoxysuccinic acid is readily prepared also by the action of methylic iodide on the silver salt, and the substance thus procured is identical with that obtained directly from methylic maleate and fumarate. Silver methoxysuccinate prepared by precipitating a solution of ammonium methoxysuccinate with silver nitrate and drying at a temperature below 100°, is heated with excess of methylic iodide, using a reflux condenser. The syrupy liquid which is left on filtration and evaporation crystallises at once when a crystal of methyl methoxysuccinate is added to it.

The substance, when recrystallised from ether and dried in a vacuum, yielded the following results on analysis, the preparations used for analyses I and II being those obtained direct from methylic fumarate and methylic maleate respectively:—

I. 0·2655 gram substance gave 0·1623 gram H_2O and 0·4624 gram CO_2.

II. 0·2915 gram substance gave 0·1792 gram H_2O and 0·5070 gram CO_2.

	Calculated for $C_7H_{12}O_5$.	Found. I.	Found. II.
C	47·73	47·50	47·44
H	6·82	6·79	6·83
O	45·45	—	—
	100·00		

Methoxysuccinamide.—Methylic methoxysuccinate was dissolved in a methyl alcohol solution of ammonia, and the mixture left in a stoppered bottle for a week. Hard, transparent crystals gradually formed, adhering firmly to the glass. The substance, being dried over sulphuric acid and submitted to analysis, was found to have the composition of methoxysuccinamide.

I. 0·3187 gram substance gave 0·2052 gram H_2O and 0·4785 gram CO_2.

0·1325 gram substance gave 22·1 c.c. N at 18° and 757 mm. bar.

II. 0·2253 gram substance gave 0·1455 gram H_2O and 0·3410 gram CO_2.

0·2832 gram substance gave 45·9 c.c. N at 16° and 760 mm. bar.

	Calculated for $C_5H_{10}N_2O_3$	Found.	
		I.	II.
C	41·10	40·95	41·28
H	6·85	7·15	7·17
N	19·18	19·53	19·19
O	32·87	—	—
	100·00		

The substance is soluble in water and in hot alcohol, insoluble in ether, and melts at 175°.

Methoxysuccinic Acid.—The constitution of the acids obtained by the addition of the elements of alcohol to fumaric and maleic acids was inferred (*loc. cit.*) from the fact that ethoxysuccinic acid yielded succinic acid when acted upon with fuming hydriodic acid. We have submitted methoxysuccinic acid to similar treatment, and find that it undergoes the same change, though apparently a somewhat higher temperature is required for the reaction. After heating the acid in a sealed tube with fuming hydriodic acid at 120°, no succinic acid could be detected, but when the mixture was heated at 160—170°, a crystalline crust of minute needles was formed in the tube. The substance, having been separated from the liquid by filtration, treated with carbon bisulphide and recrystallised from hot water, had the melting point 182—184°, and gave on analysis 40·37 per cent. of carbon and 5·26 per cent. of hydrogen; the corresponding numbers calculated for succinic acid being respectively 40·68 and 5·08.

In one of the communications to this Journal, already referred to (Trans., 1885, **47**, 861), the addition of the elements of alcohol to fumaric and maleic ethers was attributed to the agency of an unstable compound of the ethereal salt with sodium alkylate, having in the case of the methyl compounds the constitution represented by one or other of the formulæ

$$\begin{array}{l}\mathrm{CHNa{\cdot}COOCH_3}\\ |\\ \mathrm{CH(OCH_3){\cdot}COOCH_3}\end{array}, \qquad \begin{array}{l}\mathrm{CH{\cdot}COOCH_3}\\ \|\\ \mathrm{CH{\cdot}C(OCH_3)_2{\cdot}ONa}\end{array}.$$

We were inclined at one time to think that the intermediary compound probably had the constitution represented by the first of these two formulæ, and in a discussion, some years ago, of the mode of formation and constitution of acetoacetic and succinylosuccinic ethers, by A. von Baeyer and Geuther, prominence was given to this view, as bearing on the general question of the existence of sodium derivatives of ethereal salts, in which sodium is directly united to carbon. Geuther justly pointed out that the reactions of fumaric and maleïc ethers referred to, more particularly the reaction between dry sodium ethylate and ethylic fumarate, had been too imperfectly studied to admit of definite conclusions being drawn from them. The effect of sodium alkylate in causing an interchange of alcoholic radicle between an ethereal salt and an alcohol, which we have more recently described, and Claisen's observations on the action of sodium ethylate on ethylic benzoate, support the view that it is probably a compound of the kind represented by the second formula, which is the active agent in causing the addition of alcohol to the ethereal salts of unsaturated acids.

The remark of Geuther, to which we have referred, induced us at the time to undertake the investigation of the action of dry sodium methylate, and of alcoholic sodium methylate, aided by heating, on methylic fumarate. The reactions were in every case very complex, and we could not obtain well-defined products from them. We take the opportunity, however, of giving a brief summary of the results of our experiments.

When methylic fumarate was added in molecular proportion to dry sodium methylate suspended in anhydrous ether, and the mixture shaken, the fumarate disappeared, and a solid sodium compound in the form of a yellow powder was produced, from which, by means of cold dilute acids, we obtained a viscous oil soon solidifying to a light-coloured resin. The substance formed deep-yellow solutions with caustic alkalis, from which it was again precipitated by the addition of acid, and its alcoholic solution gave intense violet colours with ferric chloride, a property retained by the substance even after being fused with solid caustic potash. No phenylhydrazine or metallic or other derivatives of definite composition could be obtained by the methods usually employed with ketonic ethereal salts.

When the proportion 2 mols. of sodium ethylate to 1 mol. of methylic fumarate was taken, the resulting sodium compound yielded a viscous oil which did not solidify.

When molecular proportions of methylic fumarate and alcoholic sodium methylate were heated on the water-bath for an hour, on acidifying and extracting with ether no methylic methoxysuccinate was obtained, but a greenish-yellow oil, which gave an indigo-blue colour with ferric chloride. or deep violet in the presence of alcohol.

When sodium methylate in alcoholic solution, in the proportion of 2 mols. of the methylate to 1 mol. of fumarate, was used, and the mixture was heated for some hours on the water-bath, and then poured into ice-cold, dilute sulphuric acid, an olive-green, amorphous solid was precipitated. 50 grams of methylic fumarate yielded 40 grams of the powder dried on filter paper. The substance was soluble in benzene, ether, and alcohol, the latter solution giving an intense violet colour with ferric chloride. Analysis of the substance gave the results which follow, the substance used in analyses I and II being got by dissolving the green powder in ammonia and precipitating with acid, that used in III and IV by precipitating its solution in benzene by the addition of light petroleum. The yellowish-white powder thus obtained was in each case dried in a vacuum till constant in weight.

I. 0·2125 gram substance gave 0·0910 gram H_2O and 0·4005 gram CO_2.
II. 0 2320 gram substance gave 0·0987 gram H_2O and 0·4342 gram CO_2.
III. 0·2063 gram substance gave 0·0935 gram H_2O and 0·3877 gram CO_2.
IV. 0·2107 gram substance gave 9·0930 gram H_2O and 0·3981 gram CO_2.

	Calculated for $C_{11}H_{12}O_7$.	Found.			
		I.	II.	III.	IV.
C	51·56	51·40	51·04	51·25	51·53
H	4·69	4·76	4·73	5·04	4·90
O	43·75	—	—	—	—
	100·00				

The substance is evidently a condensation product produced by the elimination of alcohol, probably a diketonic ethereal salt of the composition $C_{11}H_{12}O_7$, formed by the abstraction of 3 mols of methyl alcohol from 2 mols. of methylic methoxysuccinate, or of 2 mols. of methyl alcohol from 1 mol. of methylic fumarate and 1 mol. of methylic methoxysuccinate. When the yellow alcoholic solution of the substance is treated with chlorine or bromine, the solution becomes of a bright scarlet or magenta colour which disappears on the further addition of the reagent. Shaking with excess of bromine-water converts the substance into an amorphous, lemon-yellow powder containing bromine; this dissolves in absolute alcohol and in pure benzene to a pale yellow solution, but in alcohol containing traces of water and in commercial benzene to bright magenta-coloured solutions. The colour disappears from the alcoholic solution on boiling, and reappears on cooling; when the alcohol evaporates, the substance regains its original yellow colour. These curious changes of colour suggest the tautomeric changes characteristic of ethyl succinylosuccinate and its derivatives. Numerous attempts to obtain crystalline derivatives from the original product of the reaction and from the bromine compound alluded to were all unsuccessful, and no simple formula for the latter substance could be deduced from the results of its analysis.

Our experiments therefore afford no proof of the formation of a simple derivative of ethyl succinate in which sodium is directly united to carbon, such as is represented by the first of the above-mentioned formulæ. A compound of the second formula is probably produced, from which, in the presence of alcohol, methylic methoxysuccinate is formed; the latter then undergoes condensation under the action of the alcoholic sodium methylate aided by heat, with the formation of the sodium derivative of a complex ketonic ethereal salt.

Ethereal Salts of Acrylic Acid.

Acrylic acid, like fumaric and maleïc acids, when heated with an aqueous solution of sodium hydrate, unites with the elements of water and yields hydracrylic acid. It seemed, therefore, likely that the ethereal salts of acrylic acid would resemble the ethereal fumarates and maleates in their action with alcohol and sodium alkylate, and that they would produce alkyloxypropionic salts. This was found to be the case.

The methylic and ethylic acrylates used in our experiments were prepared from dibromopropionic acid (procured from allyl alcohol), in accordance with the directions of Caspary and Tollens (*Annalen*, **167**, 247). The method is tedious, and gave in our hands only a small yield of the ethereal acrylate. 120 grams of allyl alcohol yielded 10 grams of methylic acrylate boiling at 80—85°; 70 grams of the alcohol yielded only 5 grams of the ethylic salt. Owing to the difficulty of obtaining these acrylic salts, our experiments were conducted on a limited scale.

Methylic Acrylate and Methyl Alcohol.—A mixture of 10 grams of methylic acrylate with 15 grams of methyl alcohol, in which 0·27 gram sodium had been dissolved, was left at the ordinary temperature for two hours, and then heated for some time on the water-bath, using a reflux condenser. As the mixture was found to have become neutral, another 0·27 gram sodium in alcoholic solution was added, and the heat of the water-bath applied again for an hour, after which the liquid still remained faintly alkaline. The quantity of sodium used relatively to that of ethereal salt amounted to one-fifth of an atomic proportion. Water was added, and the mixture shaken with ether. The ethereal extract, having been dried with potassium carbonate, yielded by fractional distillation 4 grams of an oil which boiled at 140—145°. As the results of analysis showed that the liquid probably contained alcohol, it was treated with calcium chloride and again distilled, after which the analysis of the substance gave a percentage composition agreeing pretty closely with that of methylic methoxypropionate.

I. 0·2110 gram substance gave 0·1629 gram H_2O and 0·3881 gram CO_2.

II. 0·2173 gram substance gave 0·1705 gram H_2O and 0·4031 gram CO_2.

	Calculated for $C_5H_{10}O_3$.	Found. I.	Found. II.
C	50·85	50·16	50·59
H	8·47	8·58	8 72
O	40·68	—	—
	100·00		

The aqueous solution from which the methylic methoxypropionate had been removed contained the sodium salt of the same acid. The acid was obtained by acidifying the solution with sulphuric acid and extracting with ether, but as it did not solidify it was converted into the calcium salt; the latter, on evaporation of its aqueous solution, was obtained as a gum which dried up on standing over sulphuric acid to a slightly coloured, brittle, deliquescent resin.

0·4850 gram substance dried at 105° gave 0·1958 gram $CaCO_3$.

	Calculated for $C_8H_{14}O_6Ca$.	Found.
Ca	16·26	16·15

Ethylic Acrylate and Ethyl Alcohol.—5 grams of ethylic acrylate were added to 13 grams of ethyl alcohol in which 1·1 grams of sodium had been dissolved, the proportion of sodium used in this case being 1 atom of sodium to 1 mol. of the ethereal salt. The mixture was heated for two hours on the water-bath, using a reflux condenser; water was then added, which dissolved a white precipitate which had formed, and the solution was heated to evaporate off the alcohol and cause complete hydrolysis. By acidifying the liquid with sulphuric acid and extracting it with ether, an acid was obtained from it in the form of a slightly coloured syrup, from which the calcium salt was prepared by treatment with calcium carbonate. The salt formed a thick syrup, which, on being heated at 105°, dried up to a solid which was soluble in alcohol. It was obtained as a deliquescent, crystalline mass on adding a few drops of water to the alcoholic solution and leaving it to evaporate over sulphuric acid. The following analyses show that the substance, although not quite pure, was calcium ethoxypropionate. The substance employed for analysis was dried at 105°.

I. 0·3537 gram substance gave 0·2121 gram H_2O and 0·5432 gram CO_2; the residue weighed 0·0890 gram, and yielded

0·1285 gram $CaCO_3$, and contained therefore 0·0170 gram CO_2.

II. 0·3345 gram substance gave 0·1987 gram H_2O and 0·5109 gram CO_1; the residue weighed 0·0882 gram, and yielded 0·1220 gram $CaCO_3$, and contained therefore 0·01988 gram CO_2.

III. 0·7014 gram substance gave 0·2554 gram $CaCO_3$.

	Calculated for $C_{10}H_{18}O_6Ca$.	Found.		
		I.	II.	III.
C	43·80	43·20	43·28	—
H........	6·57	6·66	6·60	—
Ca	14·60	14·53	14·59	14·57
O	35·03	—	—	—
	100·00			

The quantities of material at our disposal were so small that it was impossible to ascertain whether the compounds formed by the addition of alcohol to the ethereal salts of acrylic acid are α- or β-derivatives of propionic acid. When acrylic acid combines with the elements of water, hydracrylic acid is produced. Judging from analogy, it seems probable that the acids formed by the addition of alcohol are β-alkyloxypropionic acids. The fact that the calcium salt which we obtained did not crystallise in the well-defined manner ascribed to calcium α-ethoxypropionate (*Annalen*, **208**, 339) gives some support to the conclusion. On the other hand, Butlerow (*Annalen*, **118**, 325) found acrylic acid and α-ethoxypropionic acid as products of the action of sodium ethylate on iodoform, and concluded that the latter acid had been produced from the former.

Ethereal Salts of Crotonic Acid.

Methylic and ethylic crotonates were prepared by heating a mixture of the acid with the respective alcohols and sulphuric acid. The ethereal salt was separated by the addition of water, shaken with sodium carbonate solution, and dried with calcium chloride. 70 grams of crotonic acid heated with 100 grams of ethyl alcohol and 25 grams of sulphuric acid gave 60 grams of ethylic crotonate boiling almost entirely at 140—142°. 50 grams of crotonic acid, 75 grams of methyl alcohol, and 18 grams of sulphuric acid gave 38 grams of methylic crotonate boiling at 119—120°.

Methylic Crotonate and Methyl Alcohol.—20 grams of methylic crotonate were added to 28 grams of methyl alcohol containing in solution 0·5 gram of sodium, equal to about one-tenth of an atomic proportion relatively to the weight of the crotonate, and the mixture was heated for some time on the water-bath. The product, by treatment similar to that employed in the case of methylic acrylate, yielded 15 grams of an oil having the boiling point 146—148°, which on analysis proved to be α-methylic methoxybutyrate.

I. 0·1885 gram substance gave 0·1535 gram H_2O and 0·3777 gram CO_2.

II. 0·2403 gram substance gave 0·1985 gram H_2O and 0·4788 gram CO_2.

	Calculated for $C_6H_{12}O_3$.	Found.	
		I.	II.
C	54·55	54·65	54·34
H	9·09	9·05	9·18
O	36·36	—	—
	100·00		

Methylic methoxybutyrate readily undergoes hydrolysis on heating with a 10 per cent. aqueous solution of sodium hydrate, yielding sodium methoxybutyrate. This salt is obtained by treating the product of hydrolysis with carbonic anhydride, evaporating the liquid to dryness, and then treating the residue with alcohol, in which the salt is readily soluble. On evaporating the alcohol, it remains in the form of a thick syrup, which solidifies on standing.

Analysis of the substance dried at 100° yielded the following results:—

I. 0·3447 gram substance gave 0·1990 gram H_2O, 0·4859 gram CO_2, and 0·1330 gram Na_2CO_3.

II. 0·2909 gram substance gave 0·1673 gram H_2O, 0·4080 gram CO_2, and 0·1132 gram Na_2CO_3.

III. 0·8278 gram substance gave 3·3161 gram Na_2CO_3.

	Calculated for $C_5H_9O_3Na$.	Found.		
		I.	II.	III.
C	42·86	42·81	42·66	—
H	6·43	6·41	6·39	—
Na	16·43	16·74	16·89	16·57
O	34·28	—	—	—
	100·00			

The zinc salt, prepared by evaporating the aqueous solution of the sodium salt with zinc sulphate and extracting the dry residue with alcohol, is a thick gum. The barium salt is a gum which solidifies on standing. The acid, obtained by acidifying a solution of the zinc salt and extracting with ether, is a liquid.

As the acid and its salts are devoid of well-marked characteristics, we prepared the acid amide with the view of obtaining a better defined derivative.

For this purpose, 6 grams of methylic methoxybutyrate were mixed with three volumes of strong aqueous ammonia and heated at 100° in a sealed tube for 12 hours. On evaporating the liquid over sulphuric acid, the amide was deposited in the form of a scaly, crystalline mass. When recrystallised from ether and dried in a vacuum, it melted at 69°, and gave the following results on analysis:—

0·1785 gram substance gave 0·1520 gram H_2O and 0·3340 gram CO_2.

0·2540 gram substance gave 26·1 c.c. N at 16° and 761 mm. bar.

	Calculated for $C_5H_{11}NO_2$.	Found.
C..............	51·28	51·03
H.............	9·40	9·46
N........	11·97	12·18
O	27·35	—
	100·00	

The acid obtained in the manner described, by the addition of the elements of methyl alcohol to crotonic acid, must be either α- or β-methoxybutyric acid. Duvillier (*Arch. Chem.* [5], 17, 548) prepared methylic α-methoxybutyrate having the boiling point 150—155°, by the action of sodium methylate on methylic α-bromobutyrate, and from the ether he obtained the acid amide in the form of slender needles which melted at 77—78°. The difference in the boiling points of the methylic methoxybutyrate prepared by Duvillier and that which we obtained is not great, and might be due to impurity in one or other of the preparations, but the amide prepared by us differs decidedly, both as regards melting point and crystalline form, from Duvillier's, and we therefore conclude that in the reactions we have described the oxyalkyl group unites with the β-carbon atom.

Ethylic Crotonate and Ethylic Alcohol.—51 grams of the crotonate were heated for half an hour with 120 grams of ethyl alcohol in which 10·1 grams of sodium had been dissolved, the proportion being in this case 1 atom of sodium to 1 mol. of ethereal salt.

The product was poured into cold dilute sulphuric acid, and the oil which separated, having been dried with potassium carbonate, was submitted to fractional distillation. No ethyl crotonate was left unacted on. The fraction boiling at 168—173°, which amounted to 16 grams, and constituted most of the oil, gave the following results on analysis :—

I. 0·2367 gram substance gave 0·2150 gram H_2O and 0·5211 gram CO_2.

II. 0·2355 gram substance gave 0·2102 gram H_2O and 0 5177 gram CO_2.

	Calculated for $C_8H_{16}O_3$.	Found. I.	Found. II.
C	60·00	60·04	59·95
H	10·00	10·09	9·92
O	30·00	—	—
	100·00		

The substance was therefore ethylic ethoxybutyrate. By employing a smaller quantity of sodium, viz., 0·08 of an atomic proportion, we obtained 18 grams of the substance from 25 grams of the crotonate.

Ethylic ethoxybutyrate undergoes hydrolysis when heated with an alcoholic solution of potassium hydrate. By neutralising the product with sulphuric acid, evaporating to dryness, and treating the residue with absolute alcohol, a solution of the potassium salt was obtained. On evaporating the alcohol, a syrup was left which, on standing in a vacuum, gradually deposited minute, very deliquescent, crystalline needles. An estimation of potassium in the substance, dried at 105°, was made with the following result :—

0·7102 gram substance gave 0·3628 gram K_2SO_4.

	Calculated for $C_6H_{11}O_3K$.	Found.
K	22 99	22·93

The alcohol with which the ethylic crotonate combines is therefore not eliminated by hydrolysis with potassium hydrate.

Ethoxybutyric acid, obtained by acidifying an aqueous solution of the potassium salt and extracting with ether, is a syrupy liquid. The calcium and barium salts are gums soluble in water and in alcohol. The silver salt is precipitated in the amorphous state on adding silver nitrate to a solution of the barium salt; it is soluble in hot water, but could not be obtained crystalline. The acid amide, prepared in the same way as methoxybutyramide, is deposited in the form of a scaly, crystalline crust, which melts at 73—75°, and after being recrystallised from ether and dried in a vacuum, at 75°. It gave the following results on analysis :—

I. 0·2583 gram substance gave 0·2325 gram H_2O and 0·5162 gram CO_2; 0·3303 gram gave 31·0 c.c. N at 12·5° and 750 mm. bar.

II. 0·2047 gram substance gave 0·1867 gram H_2O and 0·4095 gram CO_2; 0·2437 gram gave 21·9 c.c. N at 10° and 761 mm. bar.

	Calculated for $C_6H_{13}NO_2$.	Found. I.	Found. II.
C	54·96	54·50	54·56
H	9·92	10·00	10·13
N	10·69	11·11	10·89
O	24·43	—	—
	100·00		

This amide is probably identical with the amide obtained by Pinner (*Ber.*, **12**, 2057) by the action of hydrochloric acid on allyl cyanide alcoholate, and which he regards as β-ethoxybutyramide. To allyl cyanide alcoholate, Pinner assigns the formula $CH_3·CH(OEt)·CH_2·CN$. This substance, when hydrolysed with potassium hydrate, yields crotonic acid; we find, on the other hand, that ethylic ethoxybutyrate gives, by hydrolysis with potassium hydrate at 100°, not crotonic acid, but ethoxybutyric acid. When aqueous potassium hydrate was used for the hydrolysis, the acid obtained was certainly not quite pure. Thus a barium salt made from such acid gave 35·06 per cent. of barium, the number calculated for barium ethoxybutyrate being 34·34, and for barium crotonate 44·63, but no crotonic acid was deposited from the ethoxybutyric acid when it was evaporated to a syrup. It is possible that allyl cyanide alcoholate is not β-ethoxybutyronitrile, but an imide ether of the formula

$$CH_2:CH·CH_2·C(OEt):NH,$$

and that the alcohol unites with the doubly-linked carbon atoms when the substance is hydrolysed with hydrochloric acid.

Schreiner (*Annalen*, **197**, 16) prepared ethylic α-ethoxybutyrate having the boiling point 168·5°, by the action of sodium ethylate on ethylic α-bromobutyrate. The boiling point of the ether we have described approximates closely to that given by Schreiner, which would indicate that it is an α-derivative. On the other hand, the melting point of α-ethoxybutyramide is 68—69°, six degrees lower than the amides prepared by us. Further, the α-amide referred to was obtained by Duvillier (*Ann. Chim. Phys.* [5], **17**, 542) by heating the ethylic salt at 100° with alcoholic ammonia. We heated the ethylic ethoxybutyrate obtained from ethylic crotonate at 100° in a sealed tube for 20 hours with a saturated solution of ammonia in ethyl alcohol, and no amide was formed, the greater part of the oil being recovered unaltered. We therefore think it is probable that the compounds we have described are β-ethoxy-derivatives of butyric acid.

This conclusion accords with the recent observation of Fittig (*Ber.*, **24**, 84), that αβ-unsaturated acids yield β-hydroxy-acids when boiled with aqueous sodium hydrate

Ethereal Salts of various Unsaturated Acids.

Experiments on the additive action of alcoholic sodium alkylate were made with the ethereal salts of various other unsaturated acids besides those already mentioned. In some cases it was found that no permanent addition change occurred; in other cases, owing to the difficulty of obtaining pure products, the result was left in doubt. We append a short statement of our experiments.

Ethylic Methacrylate.—Calcium methacrylate was obtained by Fittig's method from citraconic anhydride, and from this the silver salt was prepared. Ethyl iodide reacts with silver methacrylate with difficulty at the temperature of the water-bath, and this method is unsuitable for the preparation of the ethereal salt. A small quantity of the substance was, however, obtained boiling at 110—120°. After completing our preparation, we found that Paul (*Annalen*, **188**, 56) had made ethylic methacrylate by the same method, except that he heated the materials in a closed tube at 100°, and was unable to distil the liquid, as it suddenly gelatinised. We succeeded in distilling the liquid. A specimen, however, which was reserved, was found, after some months, to have become transformed into a tough, colourless, transparent mass of the consistency of indiarubber.

The product obtained by the action of alcoholic sodium ethylate on ethylic methacrylate was acidified and extracted with ether. The oil left on evaporation was hydrolysed with alcoholic potash, and the product acidified and extracted with ether. The liquid acid thus obtained yielded a barium salt which did not crystallise, but solidified when dried at 100°, and gave on analysis C 34·59, H 4·94, Ba 36·50 per cent., the corresponding calculated numbers for barium methoxyisobutyrate being 36·09, 5·51, and 34·34. These results indicate that the additive action had occurred, but that the substance contained some barium methacrylate.

Ethylic Angelate.—Angelic acid was prepared from camomile oil. Puckert's method (*Annalen*, **205**, 240) gave unsatisfactory results, aqueous caustic potash having little or no action at the ordinary temperature on our sample of the oil. By Beilstein and Wiegand's modification of Pagenstecher's process (*Ber.*, **17**, 2261) we obtained

43 grams of angelic acid, melting at 44—45°, from 500 grams of camomile oil. The tiglic acid which we succeeded in separating amounted to 2 or 3 grams only.

In order to avoid the risk of the conversion of angelic into tiglic acid, ethylic angelate was prepared by the action of excess of ethylic iodide on silver angelate, dried below 100°, and finally in a vacuum. 37 grams of angelic acid yielded 24 grams of ethylic angelate boiling at 135—145°, mostly at 140—145°. When ethylic angelate was treated with alcoholic sodium ethylate in the proportion of $\frac{1}{8}$ atom of sodium to 1 mol. of angelate, an oil was obtained by extraction with ether, which was found by its boiling point, 145°, and by its yielding angelic acid on hydrolysis, to be unaltered ethylic angelate. When the proportion 1 atom sodium to 1 mol. of angelate was used, the product solidified. By treatment with acid and extraction with ether, a little tiglic acid was obtained, recognised by the melting point 65°, and an oil which, after distillation and hydrolysis, also yielded tiglic acid. A barium salt made from this acid gave on analysis 40·68 per cent. of barium, 40·92 being the percentage of barium calculated for barium angelate or tiglate. Ethylic angelate, therefore, does not unite with ethyl alcohol to form a saturated compound under the conditions of our experiment.

The conversion of angelic into tiglic acid under the conditions described is a point of some interest which we intend to investigate further.

Ethylic Allylacetate.—This ethereal salt was prepared from ethylic allylacetoacetate. We found that the latter, when heated with a relatively small quantity of *alcoholic* sodium ethylate, undergoes decomposition similar to that which is known to occur (*Annalen*, **234**, 164) with ethylic acetoacetate under similar conditions. On heating 10 grams of ethylic allylacetoacetate with 14 grams of ethyl alcohol, containing 0·13 gram of sodium in solution, at 180° in a sealed tube, the mixture still remained alkaline, and we obtained from it 5 grams of ethylic allylacetate boiling at 140—150°, the boiling point of the pure ethereal salt being 142—144°. It appeared from its mode of preparation that this substance did not unite with alcohol to form a saturated compound, but as decomposition of the additive compound might possibly have occurred during distillation, the ethylic allylacetate was heated again on the water-bath with ethyl alcohol and one-tenth atomic proportion of sodium ethylate. By hydrolysis, acidifying, and extracting with ether, a liquid acid was obtained, from which the calcium salt was made. The latter was found to contain 16·86 per cent. of calcium, the calculated percentage for calcium allylacetate being 16·81. No addition, therefore, had occurred.

Ethereal Cinnamates.—Numerous experiments were made with both methylic and ethylic cinnamates and sodium and potassium alkylates in alcoholic solution under varying conditions of proportion of materials and temperature, but no saturated compound was obtained, the cinnamic acid being recovered unaltered.

Ethylic o-(β)Ethylcoumarate.—This substance was treated with alcoholic sodium ethylate in the proportion of 1 atom of sodium to 1 mol. of coumarate, and the mixture was heated on the water-bath No additive compound was found. From the product of hydrolysis, *o*-(β)ethylcoumaric acid alone was obtained, recognised by its melting point, 133°.

Ethylic Phenylpropiolate.—This substance was prepared by Perkin's method (Trans., 1884, 174). It was distilled under reduced pressure, and boiled at 208—210° at 60 mm. When alcoholic sodium ethylate was added in the proportion of 1 atom of sodium to 1 mol. of the ethereal salt, a precipitate was formed, and the mixture became warm. By adding glacial acetic acid and water, and shaking with ether, an oil was obtained which, however, underwent decomposition when treated with caustic soda. It was probably unaltered ethylic phenylpropiolate. In another experiment in which sodium was used in smaller quantity, phenylpropiolic acid was recovered and recognised by its melting point, 137°. The ethereal salt probably forms no permanent additive compound by the action of alcoholic sodium ethylate. We purpose, however, repeating the experiment.

It appears from the results of our experiments that the ethereal salts of unsaturated acids differ greatly with respect to their capability of combining with the elements of alcohol under the agency of sodium alkylates. This capability is evidently affected by the position of the doubly-linked carbon atoms and by the nature of the atomic groups with which they are united; we are unable, however, at present to draw any general conclusion regarding the influence of these factors.

We intend to pursue the inquiry further.

XLVII.—*On Nitrification.* Part IV.

By R. Warington, F.R.S.

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As I am obliged for the present to discontinue my researches on nitrification, it is the object of the present paper to gather together the principal unpublished results which I have obtained. Many lines of investigation will be found incomplete, and some results stand in need of verification, but their publication may be of some value to other investigators. The facts I have to mention will be more conveniently grouped under distinct heads than narrated in chronological sequence. The first section deals with experiments made long ago, with more or less imperfect methods.

DISTINCTION BETWEEN THE PRODUCTION OF NITRITES AND NITRATES.

1. *Behaviour of Soil with Ammoniacal Solutions.*

The nitrification which occurs in a mass of aërated soil at the ordinary temperature is purely nitric in character, as not more than traces of nitrous acid are to be found in the drainage waters of cultivated land. When nitrites are formed in a natural soil, their origin is apparently due to the action of reducing bacteria, which, under a deficient supply of oxygen, determine a reaction between the nitrates and the organic matter of the soil.

In the early years of my investigations a good many experiments were made as to the nitrous or nitric character of the reaction produced by adding a few particles of fresh soil to solutions of ammonium chloride containing sodium potassium tartrate, potassium phosphate, magnesium sulphate, and an excess of calcium carbonate. If the solution was cold and weak (80 milligrams of ammonium chloride and the same of tartrate per litre), the nitrification was slow, but almost wholly nitric in character, traces only of nitrous acid occurring in any stage of the operation; the depth of the solution might be 5 inches without altering this result.

If a solution eight times this strength was placed under the same conditions, nitrous acid was at first produced in large quantity, but finally this was converted into nitric acid. By reducing the depth of the solution to 1 inch, the production of nitrous acid was much diminished, and that of nitric acid increased. By raising the temperature to 30° nitrification became much more rapid, the production of nitrites was greatly increased, and took place abundantly even in the case of weak solutions; but here also the nitrites were finally converted into nitrates. The rates of nitrification showed that the production of nitrites in cold, strong solutions, was not due to a deficiency of oxygen (Trans., 1879, 447).

The main point to which I would now direct attention is that under all circumstances of depth of solution and temperature examined, nitrates were the final result of the action of soil. It is, indeed, easily proved that soil possesses the power of converting nitrites into nitrates, by adding a few particles of soil to a weak solution of potassium nitrite containing the necessary phosphates, &c.: the nitrite is found after some weeks to be completely converted into nitrate.

In a series of experiments in which a clay soil from various depths was placed in a ½ per cent. urine solution with calcium carbonate, it appeared that the property of producing nitrates was possessed not only by the surface soil, but also by the subsoil from various depths extending to 4 feet below the surface. The surface soil of pasture land showed a greater tendency to produce nitrites than the surface soil of arable land.

2. *Recognition of a Purely Nitrous Agent.*

If we proceed to make a series of successive cultivations in ammoniacal solutions, starting from a culture which has yielded nitrates, we sometimes meet with an entirely different phenomenon—the power of producing nitric acid is found to be entirely lost, while the production of nitrous acid from ammonia continues with great vigour.

This fact was observed very early in my investigations (Trans., 1879, 451). On August 11, 1878, two ammoniacal solutions, JD and KD, were seeded from an old culture which had produced nitrates; when nitrification commenced, the quantity of nitrite present was from time to time determined with a solution of potassium permanganate. On November 4, nitrification was almost completed, a trace only of ammonia remaining. On March 13, 1879, 129 days afterwards, the quantity of nitrite present was undiminished; it amounted to about 92 per cent. of the ammonia originally present. After the publication of these results, the cultures in question were placed in an incubator at 30° for 52 days; they were afterwards kept in the cold for three years. No diminution in the amount of nitrites was observed.

The conclusions arrived at in 1879 are thus summarised at the end of "Nitrification, Part II."

"20. The product of nitrification is not uniform; sometimes nitrous and sometimes nitric acid is produced. A purely nitric fermentation has occurred only in the case of cold dilute solutions nitrified in the dark. In the case of strong solutions, or of nitrification at elevated temperatures, or in the light, the nitrification has been wholly or chiefly nitrous. Cold dilute solutions, in which nitrification has been long checked by the absence of a salifiable base, also assume a nitrous fermentation when a base is introduced. Further investigation is needed under this head.

"21. It does not appear that the production of nitrous acid is due to a deficiency of available oxygen; at least this is not a sufficient explanation for all the facts. The production of nitrous or nitric acid seems to depend in part on the condition of the ferment. The subject is as yet very obscure.

"22. The nitrites which are produced during nitrification sometimes pass into nitrates with astonishing rapidity during the final stage of the process, and before the ammonia has entirely disappeared. Under other circumstances, they remain unchanged for a long time after all ammonia has been consumed. Light is apparently a condition which prevents nitrites from turning into nitrates. This, like the preceding question, is at present very obscure.

"23. The nitrifying ferment in certain conditions seems only capable of producing nitrous acid, and is unable, even in the dark, of converting nitrites into nitrates."

Results similar to those obtained in cultures JD and KD were afterwards obtained in several other instances, and much labour was spent to ascertain—(1) the permanence of the nitrous agent; (2) the purity of its action; (3) the conditions of its formation. Very little of this work has been published.

At the commencement of my next communication to the Society (Trans., 1884, **45**, 637), I say that much time has been spent in "an attempt to elucidate the causes which determine the nitric or nitrous character of the final product. This special branch of the inquiry, in spite of much labour, is not yet ripe for publication." Later on (pp. 638, 639) I mention that Messrs. Schloesing and Müntz regard the formation of nitrites in a solution as determined simply by external conditions (temperature too low, and want of aëration), while my own results show that in certain cases the result is determined solely by the character of the agent introduced. "It is indeed possible to have two similar solutions, under identical external conditions, in one of which only nitrites, and in the other only nitrates are being produced."* The subject has recently assumed fresh importance in the light of new developments in the theory of nitrification. I will proceed, therefore, to give a brief account of the principal facts shown by my own experiments.

3. *The Permanence of the Nitrous Agent.*

When once the nitrifying agent has assumed the nitrous character, it ever afterwards retains it; at least, I have failed to find conditions under which the faculty for producing nitrates may be restored. In early experiments (1879—82) successive cultivations of the nitrite-yielding organism were carried out for two years in ammoniacal solutions without any alteration appearing in the product. Diminishing the depth of the solution to half an inch, so as to obtain abundant aëration of the liquid, did not hinder the formation of nitrous acid, or cause any nitric acid to be produced. The experiments were made in tumbler beakers, covered by a clock glass, over which was a closely-fitting cap of filter paper. Cultivation at a temperature of 30°, with or without a shallow depth, was equally ineffective.

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* Dr. J. H. M. Munro (Trans., 1886, **49**, 653, 659, 660) has also obtained cultures in which only nitrites were produced, and remained permanent. He found the water of a shallow well to possess this property.

The nitrite-yielding organism nitrified dilute urine and asparagine solutions, and later experiments showed that it equally attacked milk; in all cases nitrites were produced, and these remained permanently in the solution. Quite recently I have grown the nitrite-yielding organism in ammoniacal solutions containing 20 per cent. of broth; here, again, apparently only nitrites were produced. In no case has the liberal nourishment of the organism altered its properties; it has not thus obtained increased vigour and gained the power of producing nitrates.

The nitrite organism is without effect on solutions of potassium nitrite, supplied with phosphates, &c., which are rapidly converted into nitrate by soil, or by seeding from cultures which oxidise ammonia to nitric acid.

4. *The Purity of the Nitrite Product.*

I have said that the nitrous agent produces only nitrous acid. This is my belief on the evidence before me, but it is not a fact of which the absolute demonstration is easy. There is no difficulty in showing that very little nitric acid can be present; the difficulty is to decide with perfect accuracy whether there is a little or none. The experiments I now refer to were made in 1880—81.

The nitrous acid was determined volumetrically by a weak solution of potassium permanganate. As a very small quantity of tartrate was the only organic matter (besides the organisms) in my ammoniacal solutions, this method was quite suitable.

It is easy to obtain low results when determining nitrites with permanganate; indeed, the solutions cannot be mixed in the presence of an acid without a slight nitrous odour being perceived, showing that a part of the material is escaping full oxidation; and this loss may be much intensified if care is not taken as to the mode of mixing. The plan I finally adopted was to ascertain approximately (if need be, by a preliminary experiment) what amount of permanganate was required; then in a final experiment to add a somewhat greater volume of permanganate to the nitrite solution, acidifying with sulphuric acid, and allowing the whole to stand 5 minutes: the excess of permanganate was then found by adding potassium iodide, a little starch, and titrating with sodium thiosulphate.

The permanganate should always be standardised with a pure nitrite, employed as the succeeding experiments will be made; if this point is neglected, the results are sure to be low. Thus 1 c.c. of the permanganate I used had a value of 0·0001284 gram of nitrogen as nitrite when standardised with iron, but a value of 0·0001352 when standardised with potassium nitrite prepared from silver nitrite, and used as above described.

The presence of nitric acid in a nitrite solution may be ascertained by the difference between the amount of nitrous acid and the amount of total nitrous and nitric acid present; but determinations by difference can hardly be considered satisfactory when very small quantities are in question. The method I employed was, in principle, that recommended by Piccini (*Gazzetta*, 9, 395). About 5 c.c. of the nitrite solution were placed in a small beaker, urea was then dissolved in the liquid, a few drops of dilute sulphuric acid added, and the beaker then plunged into boiling water for two or three minutes: all nitrites were now completely destroyed, and it was possible to test for any remaining nitrate with diphenylamine,* or with other suitable reagents. Urea, when employed for this purpose, should always be tested with diphenylamine, as so-called "pure" urea sometimes contains nitric acid.

This method would have answered the purpose very perfectly, but for the fact, afterwards discovered, that traces of nitric acid are always found by this method, even when a pure nitrite is operated on. This I believe to be due to the decomposition of nitrous acid in the presence of water and air, as soon as it is separated from combination by the addition of a stronger acid (*Chem. News*, 1885, 51, 41).†

Only traces of nitric acid were found by the urea process in the cultures I examined. In nine solutions the nitrogen as nitric acid in one case only exceeded 1 part per million. In four instances of quantitative experiments the nitrous nitrogen averaged 97·3 per cent. of the total nitrogen. If nitric acid is in any case really present, it must occur as a bye-product, as we have seen that the nitrous agent has no power of converting nitrites into nitrates.

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* Diphenylamine, as is well known, produces its splendid violet tint both with nitrous and nitric acid; there is, however, a marked distinction in its behaviour with these acids, the knowledge of which is often of service to the chemist. If the solution of diphenylamine is not too strong, a drop of it produces little turbidity when added to water, or to a solution of a nitrate; but if a nitrite is present, a considerable cream-coloured turbidity ensues. This reaction is, I believe, well known to organic chemists. When strong sulphuric acid is dropped in after adding the diphenylamine, the violet colour appears after the first drop or two of acid when a nitrite is present, but only after a much larger addition in the case of nitrates, except the solution is very strong.

† The methods subsequently employed by P. F. Frankland (Trans., 1888, 364) are very good for ordinary purposes, but are probably open to the errors already mentioned. The determinations given of nitrites by his urea method are probably below the truth, a fact masked in Frankland's experiments, as the strength of his sodium nitrite was only ascertained by permanganate. The evaporation of a nitrite with ammonium chloride is, I think, sure to produce a trace of nitrate.

5. *Conditions which Determine the Formation, or Separation, of a Nitrous Agent.*

When a solution which has nitrified, and yielded nitrates, is employed for seeding other solutions, the relative production of nitrous and nitric acid may vary according to the concentration, the depth, and the temperature of the liquid, precisely as has been already noticed in cases in which soil itself has been employed as seed (p. 485). I have no facts, however, to show that any of these conditions continually repeated finally destroyed the power of producing nitric acid, though it is possible that this may be the case.

The earliest results apparently showed that in a series of successive cultures in ammoniacal solutions the property of forming nitrates became weakened. Also, that the age of the culture was in some cases a determining factor in the alteration of its properties; as before a certain date a culture might be able to impart to other solutions the power of producing nitrates, while after that date it was not able to do this. The following table, which shows the derivation of the first two cases of a purely nitrous agent, will illustrate these points. The composition of all the solutions employed in the first series will be found in Trans., 1878, 44; 1879, 429. Those used in the second series were quite similar.

Name of culture.	Seed employed.	Date of seeding.	Final result.
AD2	pasture soil	July 11, 1877	Nitrates.
AD	AD2	October 15, 1877	"
AL	AD2 and AD	October 15, Dec. 2, 1877	"
G	AL	May 18, 1878	"
JD and KD	AL	August 11, 1878	Nitrites.
N'4	pasture soil	September 29, 1879	Nitrates.
A2	N'4	January 8, 1880	"
5A	N'4	September 28, 1880	Nitrites.

In the second series mentioned in the table, much nitrous acid was produced in the first subculture from N'4, and the change into nitric acid took place only after a long time: the power of producing nitrates was thus much weakened before it was finally lost.

About this time Pasteur published his results on the attenuation of the virus of chicken cholera; he showed that by allowing a culture of this organism to become old the organism became of diminished energy, and when cultivated in fresh solutions continued to produce organisms of the same diminished energy. It seemed to me very probable that the diminution in power observed in the nitrifying organism was brought about in the same way; indeed, the facts then existing seemed plainly to point to this conclusion; all my earlier cultures had in fact at this time lost their power of forming nitrates. On this hypothesis, the organism producing nitrites was simply a weaker form of an original organism producing nitrates.

With the view of ascertaining whether the age of the culture was really the determining factor in its change of properties the following experiments were made:—About 400 c.c. of the weak ammoniacal solution ordinarily used at this date (80 milligrams of ammonium chloride, 80 milligrams of sodium potassium tartrate, 20 milligrams of potassium phosphate, and 10 milligrams of magnesium sulphate per litre) were placed in a wide-mouthed pint bottle, the mouth closed with cotton-wool, and the whole sterilised in a water-oven. On March 8, 1881, an excess of calcium carbonate was added, the solution seeded with about 0·25 gram of arable soil, and the bottle placed in an incubator at 30°. On March 15, the presence of nitrous acid could be detected. On March 25, the ammonia had disappeared. On March 29, the solution contained 19·4 parts of nitrous nitrogen per million. On April 8, the nitrites had entirely disappeared. On April 13, the nitrogen as nitric acid was 22·0 per million. The incubation period was thus 7 days; the period of oxidation of the ammonia to nitrous acid about 10 days; whilst about 14 days more elapsed before the nitrites were converted into nitrates. This is a perfectly normal action, regard being had to the depth of the liquid and the high temperature. Had a precisely similar bottle been kept at a temperature of 15°, no appreciable formation of nitrous acid would have occurred. The change of the nitrous into nitric acid was really very rapid, the solution containing 19·4 of nitrous nitrogen per million on March 29, and only 1·2 per million on April 5.

From the culture thus obtained I proceeded to prepare subcultures at frequent intervals, with a view of ascertaining, if possible, the date at which the power of producing nitrates ceased to exist; these subcultures were conducted at the ordinary temperature of the air, in solutions similar to that just described.

The subculture of April 28, 1881, was mainly nitric in character, the nitrous nitrogen never exceeding 4 per million; the nitrites disappeared about the same time as the ammonia.

The subculture of May 28, 1881,* was still more nitric in character, the small amount of nitrite formed at first disappearing long before the oxidation of the ammonia was complete.

The July subculture was far more nitrous; the quantity of nitrite produced was very large,* and remained undiminished for some time after the disappearance of the ammonia, but finally changed to nitrate.

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* This, and all the other subcultures, were seeded from the original culture of March 8, and not from the culture immediately preceding.

The September, October, and November subcultures gave the same result as that of July. A certain amount of change had apparently taken place in the original culture of March, as now it produced a purely nitrous reaction even in the cold; but an agent having the power of producing nitrates was still present, and the nitrites always finally disappeared.

The preparation of subcultures from the original culture of March 8 was continued for two years, but without further alteration in the character of the reaction; the power of producing nitrates was thus not extinguished by age. Further experiments were made by starting new cultures from some of the subcultures after they had acquired a considerable age, but this also was without the desired result. A shorter series of trials with the same object was commenced in November, 1881, using again arable soil (0·05 gram), and working entirely in the cold, but no culture having purely nitrous properties was obtained.

Although these numerous experiments entirely failed to justify the hypothesis that the power of producing nitrates is necessarily lost in a long series of successive cultures in ammoniacal solutions, or that it disappears as a culture increases in age, a purely nitrous organism was obtained in one experiment, and by a method which many repetitions have shown to be almost invariably successful for the purpose. The method which proved successful was the constant presence of a certain excess of disodium carbonate.

The disodium carbonate was used in two proportions, having a definite relation to the ammonium salt present. The single proportion of disodium carbonate was sufficient to satisfy the acid of the ammonium salt, and also the nitrous or nitric acid produced, so that, theoretically, the solution would become neutral when nitrification was completed. The double proportion was twice this quantity. As the solutions contained 80 milligrams of ammonium chloride per litre, the single proportion of disodium carbonate amounted to 160 milligrams, and the double proportion to 320 milligrams per litre; with the latter proportion, the liquid would remain distinctly alkaline after nitrification had come to an end.

Many experiments had been already made with the single proportion of disodium carbonate, but without any conclusive effect on the character of the nitrification. An experiment with the double proportion of disodium carbonate was commenced on October 13, 1881: the solution was seeded from the May subculture already mentioned. Nitrification was extremely slow in beginning, an occurrence which is usual in the case of alkaline solutions (Trans., 1884, **45**, 655). Owing possibly to this circumstance, the culture was neglected, but when examined after many months it was found that the ammonia had disappeared, and that nitrous acid was abundant. On February 10, 1883, a number of old cultures, including the one just named. were used as seed for fresh ammoniacal solutions, supplied only with calcium carbonate as the necessary base; the object was to see if any of these old cultures contained the nitrous organism alone. Of the cultures tried, that only which had received the double proportion of disodium carbonate was found to give a pure and permanent nitrous product.

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* At the meeting of the British Association in August, 1881, I read a short paper "On Alterations in the Properties of the Nitric Ferment by Cultivation." In this paper the change from a nitric to a nitrous action was regarded as determined by the age of the culture, and with this view all the facts which up to that date had come under my notice agreed.

Before the influence of an excess of disodium carbonate was known, various other attempts were made to alter the character of the nitrifying organism. As it appeared from the researches of Pasteur and others that the virulence of an organism was often permanently weakened by exposing it to conditions unfavourable to its existence, I tried whether exposure to excessive heat would alter the character of the nitrifying agent. Two urine solutions were seeded with similar soil, but in one case the soil had been heated with a little water in a test tube for 2 hours to the temperature of 50°. Nitrification commenced a good deal later in the solution seeded with the heated soil, but the reaction did not assume a more nitrous character. A similar experiment, in which a nitrified solution was used as seed, failed, as the heating to 50° killed the nitrifying organism. Exposure of the same culture to strong sunlight for some days also rendered it sterile.

In February, 1883, an extensive series of experiments was commenced upon the yet unsolved problem. It was determined to take, at the same time, both pasture and unmanured arable soil, to start preliminary cultures from these, and then to seed from these cultures a series of various solutions. The usual ammoniacal solution was employed, both with half (40 milligrams), and with double (160 milligrams) the usual proportion of tartrate per litre. Each proportion of tartrate was employed both with calcium carbonate as the base, and with the before-mentioned "double" proportion of disodium carbonate. Diluted milk (5 c.c. skimmed milk per litre) was also used with calcium carbonate, and with the double disodium carbonate. In one solution, both in the arable and pasture series, magnesia was omitted. Most of the first series of cultures were duplicated; in one case the liquid was shallow, and in the other deep. When nitrification was completed it was intended to use each culture as seed for a solution similar to the first, so that the accumulated effect of each kind of solution might be perceived. Finally, the samples of pasture and arable soil serving as the source of the nitrifying agent were taken in February, May, and August, and a similar series of experiments started with each; it was hoped that in this way differences, if any, in the natural condition of the soil organism, might be perceived. The general results obtained were as follows:—

The pasture soil gave a distinctly more nitrous reaction than the arable. In the preliminary cultures of the February and August soils, the nitrites remained unchanged far longer in the pasture than in the arable cultures. In the case of the August soils, the nitrites disappeared almost as soon as the ammonia in the arable culture, but remained more than 46 days after the ammonia had gone where pasture soil had been employed. The same difference of character was shown in the subcultures.

In all, out of 87 cultures, 15 gave a permanent nitrous product; of these 5 were derived from arable soil, and 10 from pasture soil.

Of the 5 arable cultures, 4 were cases in which the double proportion of disodium carbonate had been employed. Of the 10 pasture cultures, 6 had received the disodium carbonate. I have little doubt, from the experience subsequently gained, that the whole of the cultures with excess of disodium carbonate would have yielded a purely nitrous product if the first cultures had been again used as seed for fresh alkaline solutions; this repetition was made only in the first series, as the required result had been obtained without carrying the work further.

Of the cases in which 40 and 160 milligrams of sodium potassium tartrate were present, the former condition was apparently more favourable to the development or separation of a purely nitrous agent, for there were in all 5 instances of a permanent nitrous product with the smaller proportion of tartrate, and only 1 with the larger. Four milk, and 3 urine solutions, were among those in which the power of producing nitrates was lost.

The results of this large series of experiments certainly help to explain the earlier facts which had appeared so puzzling. The ease with which the organism in the earlier cultures passed into the nitrous condition was doubtless due to their having been all seeded originally with pasture soil;* the difficulty subsequently experienced in producing this change was owing to arable soil having been substituted.

The great influence of the alkali carbonate in promoting the change from a nitric to a nitrous reaction has been amply confirmed by subsequent experiments. The change may be easily brought about by conducting nitrification in dilute solutions of ammonium carbonate. The culture solution I have usually adopted, containing ammonium chloride and calcium carbonate, is far more favourable to the production of nitrates. Schloesing has recently (*Compt. rend.*, **109**, 1889, 883) mentioned excessive alkalinity of the solution as favourable to the production of nitrites, but he has never recognised that a permanent nitrous agent may be obtained by cultivation in such a solution, or, indeed, by any other means.

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* The pasture soil was in every case taken from among the roots of the grass, at a depth of 1½—2 inches from the surface.

Although the experiments I have now described have shown in what manner an organism, producing only nitrites, may be obtained from soil, they throw no light on the question whether the nitrification peformed by soil is the work of one or two organisms; whether, in fact, the nitrous organism is merely a weakened form of the original bacterium of the soil, or whether the nitrous agent has become prominent, and its work final, by the removal of the nitric agent with which it was at first associated. The question will be discussed later on in this paper, when more facts are before us.

We may here, however, usefully clear the ground of one hypothesis which has been offered in explanation of the production of nitrites in my own experiments. It has been suggested by Gayon and Dupetit (*Annales de la Science agronomique*, 1885, 229) that the nitrites in my experiments have been formed by reduction. The fact of the absolute permanence of the nitrites in solutions containing a nitrifying organism, and the fact that very shallow liquids are as suitable for this nitrite production as deep solutions, would probably negative this hypothesis; we owe, however, to Dr. Munro, two further lines of proof, which must satisfy everyone that the operation in question is not one of reduction.

Dr. Munro was the first to show (Trans., 1886, **49**, 653, 659, 660) that the production of nitrites alone would readily occur in solutions to which no organic matter had been added, and which, therefore, did not possess the conditions suitable for a reducing process. This line of proof has since been abundantly confirmed by myself and others. He also showed (*Chem. News*, **56**, 1887, 62) that the production of nitrites in an ammoniacal solution was not increased by the presence of nitrates, which remained unaffected during the reaction.

THE ISOLATION OF THE NITROUS ORGANISM.

1. *Original Description of the Nitrifying Organism.*

Schloesing and Müntz, to whom we owe the proof that the process of nitrification is determined by a living organism, claim to have separated that organism from all others, and have given a description of its appearance under the microscope (*Compt. rend.*, 1879, **89**, 891). The method used for its isolation consisted simply in the preparation of successive cultures in sterilised liquids suitable for nitrification. With the experience since obtained, it seems unlikely, though not impossible, that a pure culture would be obtained by this method: moreover, no proof of purity is given, save that the final culture contained but one kind of organism when viewed under the microscope. Their description, however, of the appearance of the organism agrees well with the characters since ascertained in cultures of greater claim to purity, and there can be little doubt that they actually observed the true nitrifying agent. What they have told us left, however, so many questions unanswered, that it was essential, for an exact knowledge of the subject, that the organism should be carefully isolated and further studied. The isolation of the organism was not only required by the bacteriologist, it was also most important that the chemist should be able to study its properties when separated from the multitude of other organisms with which it is associated in soil.

According to the original description of Schloesing and Müntz, the nitrifying organism consists of corpuscles, round or slightly elongated, of varying dimensions, largest when grown in mediums rich in organic matter, but at all times very small, occurring either singly or in pairs, multiplying by division. Müntz and Marcano (*Ann. Chim Phys.* [6], **10**, 1887, 563) have since stated that the nitrifying earths of Venezuela contain in abundance an organism three or four times larger than that just described, but after cultivation in weak sewage the dimensions approximate to those of the French organism. The tropical organism apparently possessed peculiarly energetic nitrifying powers.

Duclaux (*Chim. biologique*, 1883, 708; *Fremy's Encyclopedia*, **9**) has made a careful study of the nitrifying organism as separated by the French chemists. He speaks of it as having a feeble refractive power; as not being truly round or oval, but more like a bacillus broken short, with all its angles rounded; and further, as exhibiting a difference of size in the same culture greater than that shown by any other organism he is acquainted with. He naturally suggests that more than one species may be present.

2. *Earlier Rothamsted Work.*

My own work was originally undertaken solely from a chemical point of view, and previously to 1887 I had not the command of a microscope suitable for bacteriological work; some facts relating to the development of the organism in nitrifying solutions were, however, observed, and a few microscopic observations were made by friends to whom materials were submitted.

It was soon noticed that when nitrification had energetically set in, the small quantity of precipitated calcium carbonate placed at the bottom of the bottle assumed a curdled appearance, hanging together in flakes. When the supply of calcium carbonate was insufficient, it was entirely dissolved as nitrification proceeded, and small flocks of gelatinous matter remained at the bottom of the culture. The same gelatinous matter could be produced by treating the curdled sediment with dilute hydrochloric acid. Both the curdled sediment, and the gelatinous matter were microscopically examined by Mr. G. H. Makins, of St. Thomas's Hospital, a former pupil of Dr. Klein. Under date April 20, 1883, I find in my note book, "Solution and sediment examined. Masses of highly refractive corpuscles, circular, sometimes single, sometimes two in contact, often in a mass of zoogloea. These bodies not altered by HCl, not stained by iodine, stained feebly by alkaline methyl-blue."

In 1884, nitrification was started in several pretty strong solutions of ammonium carbonate (Trans., 1884, **45**, 658), no solid calcium carbonate being present. These alkaline solutions remained quite transparent during nitrification. A good while after the conclusion of the experiment, clear, gelatinous flocks were observed at the bottom of the solution. Circumstances here seemed peculiarly favourable to the occurrence of the nitrifying organism in tolerable purity. The gelatinous matter was stained and examined by Mr. Makins; it consisted of a mass of small, generally oblong corpuscles, very rough looking and ill-defined. No other forms were seen.

In 1886 I went for a short time to study under Dr. Klein, at the Brown Institution. The culture containing the gelatinous matter just named was taken with me. The substance was spread on gelatin; a small bacillus was obtained, which I have called *B. tardecrescens* (Trans., 1888, **53**, 731). This bacillus was introduced into suitable ammoniacal solutions, and found to possess no nitrifying power.

In the light of recent work, it is easy to see that the gelatinous matter I examined was in fact the nitrifying organism. Winogradsky, in his first memoir on nitrification (*Ann. de l'Institut Pasteur*, 1890, 213), has described the formation of these gelatinous clots, and from them he finally obtained the organism in a pure condition. The ill success which attended my attempts at isolation was due to the now well recognised fact that the nitrifying organism will not grow on gelatin.

The next stage of my investigation has been already described to the Society (Trans., 1888, **53**, 727); it consisted in the examination of a number of organisms, including several reputed to possess nitrifying powers, with the view of ascertaining whether they were capable of nitrifying ammonia. The investigation was from this point of view entirely unsuccessful. Dr. P. F. Frankland, and several other investigators, have met with the same result.

3. *Recent Rothamsted Work.*

In March, 1889, I commenced a systematic attempt to isolate the nitrifying organism; I was wholly unaware that Dr. P. F. Frankland was occupied with the same subject. The point first aimed at was to prepare a series of cultures of the nitrifying organism under conditions unfavourable to the development of ordinary bacteria, and thus either to effect their final exclusion, or at least so to reduce their proportion that the final separation of the nitrifying organism should be made much easier. The condition I chiefly relied on for effecting this separation of organisms was the exclusion of organic matter from the solutions. Munro had shown the possibility of conducting nitrification in solutions to which no organic matter had been added; experiments of my own, to be described further on (p. 510), had confirmed this fact. It will be convenient if I mention at starting the nature of the media employed.

Media Employed.—As microscopic examinations of the solutions would be necessary, I determined to discard my old culture fluid containing ammonium chloride and solid calcium carbonate, and to substitute a solution of ammonium carbonate; a clear solution without sediment was thus obtained. The composition of the solution was as follows:—

Water	1000·00
Ammonium carbonate	0·25
Ammonium chloride..........	0·50
Potassium phosphate	0·04
Magnesium sulphate..........	0·02
Calcium sulphate	0·02

The ammonium chloride was merely added to prevent the precipitation of magnesium and calcium phosphate. The solution was placed in wide-mouthed stoppered bottles; these were adopted to prevent loss of the ammonium carbonate. The bottles were half filled. After sterilising and seeding, they were covered with paper caps, and placed in an incubator kept at about 22°.

Besides other ordinary liquid media, a special one was prepared containing the soluble organic matter of soil. An arable soil was exhausted of nitrates by the application of cold water on a vacuum filter; the soil was then boiled with water and filtered; the clear amber-coloured solution obtained then received ammonium chloride, phosphates, &c.

A considerable variety of solid media was employed in the course of the investigation. The ordinary 10 per cent. gelatin, made with beef broth and peptone (Gelatin P); a 10 per cent. urine solution, solidified with 6 per cent. of gelatin (Gelatin U); a solution of 1 gram of asparagine, 0·5 gram sodium acetate, 0·5 gram potassium phosphate, 0·2 gram magnesium sulphate, 0·2 gram calcium sulphate per litre, solidified with 6 per cent. gelatin (Gelatin As). The last two with 1 per cent. of agar-agar substituted for the gelatin (Agar U, Agar As). A solution of 0·4 gram ammonium carbonate, 0·2 gram potassium phosphate, 0·1 gram magnesium sulphate, 0·1 gram calcium sulphate, solidified with 6 per cent. gelatin, or 1 per cent. agar-agar (Gelatin AC, Agar AC). All these media were made faintly alkaline. Later on the ordinary nitrifying solution, containing ammonium chloride and solid calcium carbonate, was solidified with 6 per cent. gelatin (Gelatin ACH).

The object of employing these different media was to supply, if possible, the conditions most favourable to the growth of the nitrifying organism.

First Series of Experiments.

While waiting for the main series of cultures to be sufficiently advanced for examination, some work was done with a culture in the ordinary ammonium chloride solution, seeded from a culture two years old. The culture examined was a third successive culture in solutions free from organic matter; the product of nitrification was nitrite. The sediment in this culture was examined by streak and plate cultivation on Gelatin U, Gelatin AS, and Agar U. The result was the isolation of two bacilli, which I have called *B. patulus*, and *B. oleosus*. These, and all the other separated organisms obtained in this investigation, I hope to describe in a future paper.

The trials of the nitrifying power of these two bacilli will be mentioned further on (p. 501).

Second Series of Experiments.

The first culture in this, the principal series of experiments, was started on March 28, 1889, with a little unmanured arable soil. normal nitrification occurred, nitrates being finally produced.

Second cultures, seeded from the first, were started on May and on June 27. The solution used in this and subsequent cultur was the ammonium carbonate solution already described. The pr duct of the nitrification in these cultures was only nitrite; the power of producing nitrates was thus already lost.

A third culture was started on August 16. A fourth on September 19. A fifth on October 3. A sixth on October 25. None of these cultures exhibited any turbidity.

Several of these cultures were subjected to microscopical examination. The lens used was a Leitz' $\frac{1}{20}$ immersion, giving a magnification of 800 diameters. In some cases, a few sterilised cover-glasses were placed at the bottom of the bottle in which nitrification took place. At the end of nitrification, the liquid was removed with a pipette, the bottle and cover-glasses were dried at 35°, and the cover-glasses taken out and stained. This plan was proposed by Mr. G. H. Makins; it was suggested by the fact that the nitrifying organism always collects in large numbers on the bottom of the vessel in which it grows. It is interesting to note that the organisms in the bottle lost all nitrifying power by drying at 35°; when the bottle was refilled with a fresh ammoniacal solution no nitrification took place.

The sunk cover-glasses were found covered with masses of corpuscles, usually oval, and having a length generally exceeding 1 μ; the other forms present were in very small proportion. Stained preparations made from the nitrified solutions showed comparatively few organisms. The forms met with in the whole of this series of examinations were: 1. The corpuscles already mentioned. The larger ones were frequently rough in outline, reminding one of the rough rounded masses of a siliceous sea sand; these did not stain deeply. There were usually a few smaller oval corpuscles, regular in form, and always longer than broad. 2. Some very small circular organisms, often appearing as mere points, staining much more darkly than the preceding. 3. A few slender bacilli staining faintly. 4. Occasionally forms like *c*, *c*, *s*. I did not feel certain that these were a distinct organism, but thought they might be mere broken shells of the large corpuscles.

The third, fifth, and sixth cultures were examined as to the growths they would yield on gelatin and agar. Following Klein's method, a loop of platinum wire was dipped into the nitrified solution and then rubbed over a sloping surface of gelatin in a test tube; by this method the organisms grew as distinct colonies, as in a plate ultivation. Plate cultivations were also made in the ordinary way. As no actively liquefying organism was present, it was possible to ontinue the observation of these cultures for many weeks. All the ltures gave an abundant growth on gelatin. The two bacilli arated during the first series of experiments were not found in se purer cultures. A small bacillus, staining somewhat feebly, s practically the only organism obtained. I have called it

B. frugi. A liquefying coccus, and a torula were obtained in the course of plate cultivations; but as only single colonies of each occurred, they were probably of atmospheric origin; nevertheless their power of causing nitrification was thoroughly tested.

The results of the gelatin and agar cultures appeared remarkable; although the composition of these media had been specially arranged, so as to agree as far as possible with the conditions suitable for the growth of the nitrifying organism, no growths were obtained on gelatin or agar-agar corresponding to the oval corpuscles which formed by far the most abundant organism in the nitrified solutions. Since, however, several of the solutions yielded apparently no organisms on gelatin save the small bacillus, and yielded this abundantly, it seemed possible, as was suggested at the time by Dr. Klein, that we had to do with a polymorphic organism, and that the bacillus obtained was really the nitrifying agent.

Each of the five organisms which had been separated from nitrified solutions, including the two which were more probably atmospheric contaminations, were sown into solutions suitable for nitrification—1. The usual ammonium chloride solution. 2. A similar solution containing soil-extract (p. 498). 3. An ammonium carbonate solution. 4. A 1 per cent. urine solution. These solutions were seeded both with the solid organisms obtained from the surface of gelatin, and with broth cultures of these organisms. In some experiments mixtures of several, sometimes of all five organisms were introduced, it being thought possible that nitrification was a complex reaction effected by the joint action of several agents. Besides the separated organisms, the growths on gelatin obtained immediately from the nitrified solutions were employed. In no single case in the whole series of trials did any nitrification take place.

As growth on the surface of gelatin took place under conditions very different from those which occurred when the organism was submerged in an inorganic solution, it was thought possible that the power of nitrification might be lost by cultivation on gelatin, and could only be gradually regained. The gelatin cultures were, therefore, sown in broth; the broth cultures were used as seed for an ammonium carbonate solution containing 20 per cent. of broth; these cultures employed to seed similar solutions containing 5 per cent. of broth; these to seed solutions with 1 per cent. of broth; these to seed the usual inorganic solution of ammonium carbonate. In no case was nitrification obtained.

Attempts were also made to obtain nitrification from the gelatin cultures by seeding them on to a moist, well aërated, solid medium, the object being to imitate the conditions occurring in a natural soil. Stoppered bottles were half filled with small pieces of marble free from dust; the marble was moistened with an ammonium carbonate solution containing 1 per cent. of broth; the solution did not cover the broken marble. When sterilised, these bottles were seeded from the 5 per cent. broth cultures mentioned in the preceding paragraph. In no instance was nitrification obtained.

In a few cases the gelatin cultures prepared from the nitrified solutions were grown out of contact with air, the solution being applied to the lower part of a sloping surface of gelatin, and then the upper portion of the gelatin carefully melted and allowed to run over the seeded surface. Growths were obtained, but they failed to yield nitrification.

The fifth and sixth of the successive nitrifying cultures in inorganic solutions were sown on November 19, 1889, in weak broth, at a temperature of 20°. The broth became turbid in 6 days. When 18 and 20 days old, stained preparations were made, both from the liquid, and from the white deposit at the bottom of the test tubes. Some of the stained preparations seemed to consist entirely of *B. frugi*, in others a longer bacillus was also present. None of the oval corpuscles were seen, but the deeply stained, minute dots mentioned above were certainly present.

The fifth and sixth cultures were also sown in a solution of ammonium carbonate containing 20 per cent. of broth. These solutions actively nitrified. From these, solutions containing 5 per cent. broth were seeded. From these, solutions containing 1 per cent. broth were seeded. From these, cultures in solutions of ammonium carbonate were prepared. The whole of these solutions nitrified readily; the solutions were always turbid. Stained preparations showed that the bacilli diminished as the proportion of broth decreased, while the deeply stained minute dots became more manifest. None of the oval corpuscles were seen.

Trials with the Dilution Method.

While the gelatin cultures obtained from the nitrified solutions were being examined, an attempt was made to separate the nitrifying organism from the others associated with it by means of the well-known dilution-method. One part of the third successive culture in the ammonium carbonate solution was mixed with 500 parts of boiled water, and one drop from a capillary tube was added as seed to each of five bottles containing the ammonium carbonate solution. This was done on September 28, 1889. After 41 days, solution No. 5 was found to have nitrified, the others showed no change. After 91 days, Nos. 2 and 3 were found nitrified. Two solutions did not nitrify; it therefore appeared as if the dilution used had been sufficient.

The three solutions which nitrified all gave growths on gelatin. Growths took place more speedily on Gelatin U and AS than on Gelatin P. The organisms obtained on gelatin were sown in appropriate liquid media, but no nitrification was obtained.

On January 14, 1890, 10 tubes, containing an ammonium carbonate solution with 5 per cent. broth, were each seeded with one drop of a dilution to 1/1000 of a cultivation in ammonium carbonate and 20 per cent. broth, seeded from the sixth successive culture of the original ammonium carbonate series. Of these 10 solutions none nitrified.

On March 13, Prof. P. F. Frankland and Mrs. Frankland communicated to the Royal Society a paper on "The Nitrifying Process and its Specific Ferment" (*Phil. Trans.*, B, 1890, 107). They had started, like myself, by preparing a successive series of cultures (24) in an inorganic ammoniacal solution. From these cultures they had obtained growths on gelatin, none of which possessed any nitrifying power. They had finally, after many trials, succeeded, by using a dilution of one in a million, in obtaining a nitrified culture which gave no growth on gelatin, and which they believed contained the nitrifying organism in a pure state. In a note published in the *Chemical News* of March 21, I briefly stated my own attempts to isolate the nitrifying organism up to that date.

On April 16, 1890, I made a fresh attempt with the dilution method. A subculture from solution No. 2 of the first dilution series was diluted to 1/1,000, 1/10,000, 1/100,000, and 1/1,000,000; each of these dilutions was seeded into five stoppered bottles, containing an ammonium carbonate solution. The bottles were placed in an incubator, and maintained at about 22°. The solutions were tested up to 190 days, but not one of them nitrified.

On considering the possible cause of failure in the last two attempts I had made with the dilution-method, it occurred to me that it might be due to the alkalinity of the ammonium carbonate solution employed. It was quite true that this solution was easily nitrified when seeded in the ordinary way, but as alkalinity, when beyond a trifling amount, is a condition which hinders nitrification ("Nitrification, Part III," Trans., 1884, **45**, 653), it seemed possible that it might prevent it altogether when the nitrifying agent was reduced to a very few organisms. In former experiments on the distribution of the nitrifying organism in the subsoil (Trans., 1887, **51**, 118), I had found that the addition of gypsum to the diluted urine employed enabled me to detect the presence of the nitrifying organism by its action on the solution at far greater depths than when the urine solution contained no gypsum, and therefore became alkaline before nitrification. This fact had not been forgotten in preparing the solutions for the last series of trials by the dilution-method; the strength of the ammonium carbonate solution had been reduced to one-half for the two stronger dilutions, and to one-quarter for the two weaker. I now resolved to abandon the ammonium carbonate, and to return to my old ammonium chloride solution, containing solid calcium carbonate. The solution employed by Frankland was of a similar nature. My solution contained in one litre:—

Ammonium chloride	0·20 gram.
Potassium phosphate...........	0·06 „
Magnesium sulphate	0·03 „
Calcium sulphate..............	0·03 „

This solution was placed in 20 stoppered bottles, which were half filled. The bottles were divided into four series, A, B, C, D, each of five bottles, which were respectively seeded with one drop from a capillary tube of dilutions to 1/1,000, 1/10,000, 1/100,000, and 1/1,000,000 of a second subculture of No. 3 in the first dilution series. The experiment commenced on June 3, 1890.

Tested after 35 days, no nitrification had occurred. After 66 days, nitrification was in active progress in A1, A4, A5, and had just commenced in B1, B2, B5. After 91 days, nitrification had commenced in B3. After 115 days, nitrification was found in progress in C3, C5, and D4. Nitrification thus occurred in 10 solutions. No other solutions nitrified.

Each of the nitrified solutions was spread on gelatin, both Gelatin P and Gelatin U being employed. It was found, as before, that growth took place far more easily on Gelatin U than on Gelatin P; indeed several solutions gave no growth on the 10 per cent. gelatin-peptone, which yet after eight or nine days produced a considerable growth on the 6 per cent. gelatin-urine. On ascertaining this fact, the whole of the remaining testings were conducted with Gelatin U.

Out of the 10 nitrified solutions there were three, B3, C3, and D4, which gave no growth on Gelatin U, either when spread upon the surface, or when introduced into the substance of the jelly. Thus, early in October, 1890, I became possessed of three solutions which probably contained the nitrifying organism in a pure condition. I had no time to ascertain by a further extension of the dilution-method whether these cultures contained more than one organism; I at once proceeded to experiment with them.

After the publication of Frankland's paper, and before my own successful result, M. S. Winogradsky commenced the publication of his "Recherches sur les organismes de la nitrification" (*Ann. de l'Institut Pasteur*, 1890, 213). In his first memoir, he describes the method employed for isolating the nitrifying organism. After a series of cultures in an inorganic ammoniacal solution, by which the organisms growing upon gelatin were reduced to a single species, he collected the gelatinous clots which appeared at the bottom of the culture vessel, washed them, and spread them upon gelatin. After 10 days, he observed where no growth had taken place, and from these places proceeded to seed fresh ammoniacal solutions. He succeeded in this way in obtaining actively nitrifying cultures which gave no growth on gelatin. In a fourth memoir, recently published, he describes a better plan of isolation by growth on the surface of gelatinous silica. A solution of dialysed silica is concentrated till the addition of a saline solution determines its gelatinisation. The solution of silica is then poured into dishes, and rapidly mixed with one or two volumes of a solution containing ammonium sulphate, potassium phosphate, magnesium sulphate, calcium chloride, and sodium carbonate (or magnesium carbonate). The mixture becomes solid in 15 minutes. On this medium apparently all the organisms which flourish in inorganic solutions can be grown, but no others. The nitrifying organism gives, according to Winogradsky, very characteristic colonies upon silica.

PROPERTIES OF THE NITROUS ORGANISM.

The organism isolated by the dilution-method converts ammonia into nitrous acid only; it is, in fact, the agent with which we have become familiar in the earlier part of this paper. Frankland had arrived at the same result. It was, indeed, to be expected, as only nitrites were produced in the cultures from which it was separated.

With the pure organism, a number of solutions of potassium nitrite, containing phosphates, &c., were seeded. Some of these solutions were supplied with monosodium carbonate and carbonic acid, others with calcium acetate, the object being to supply the conditions most favourable for the oxidation of the nitrite (see pp. 512, 519). In no case was any diminution of the nitrite perceived.

Some experiments were also made to test the reducing power of the organism. Müntz apparently thought it possible, from facts which he observed, that the nitrifying organism when not in contact with air might act as a reducing agent. Two test-tubes, about two-thirds filled with broth containing calcium nitrate, were seeded with the nitrous organism on March 26, and kept at 22°. The solutions were tested on May 9, but no nitrite was present. Stained preparations proved that the nitrous organism was present, though not abundantly. I may here mention that none of the bacilli growing with the nitrous organism in the inorganic ammoniacal cultures has any power of reducing nitrates to nitrites.

I am unable to verify Frankland's statement as to the behaviour of the nitrous organism in broth. He says, "On inoculating from the pure nitrifying solutions into broth, the latter develops after a considerable time (about 20 days at the ordinary temperature), a very characteristic growth, the liquid becomes turbid, a very thin, whitish pellicle forms on the surface, and afterwards a considerable amount of glutinous deposit collects on the bottom, the whole liquid in fact becomes highly viscous, and adheres to a needle in long strings." I have in 24 instances seeded test tubes of broth with the pure nitrous organism. The broth was made with 1 lb. of beef to a litre of water. It was employed both neutral, and of various degrees of alkalinity. The cultures were kept at 22°. In no case did the broth become turbid, nor did any visible growth appear. As already mentioned, the organism could be found in the broth, but it apparently had not greatly multiplied.

It has been already shown, by the experiments made during the isolation of the nitrous organism, that it refuses to grow on gelatin. When the ammoniacal solution, in which the organism freely grows, was solidified with 6 per cent. of gelatin, no growth was obtained by seeding this with the pure nitrous organism.

It was of great interest to ascertain whether the nitrous organism was itself capable of attacking nitrogenous organic bodies, or whether it was necessary that other organisms should first reduce these to ammonia before nitrification could take place. On obtaining the organism in a pure state, experiments were at once started in solutions containing urea, urine, asparagine, and milk. The urine was a 1 per cent. solution. The milk contained 5 c.c. of sweet skim-milk per litre. The urea solution contained—urea, 0·50 gram; potassium phosphate, 0·10 gram; magnesium sulphate, 0·10 gram per litre. The asparagine solution contained—asparagine, 0·2 gram; potassium phosphate, 0·10 gram; magnesium sulphate, 0·10 gram per litre. All the solutions received precipitated calcium carbonate before sterilisation. Two experiments, each seeded from a different culture of the nitrous organism, were made with each solution at the temperature of 22°. Afterwards a more extensive series of experiments was started with similar solutions at the same temperature, six bottles of each solution being taken, each six containing three pairs, each pair seeded from the same source, but one bottle receiving calcium acetate, 0·50 gram per litre. The results of the two series may be summarised together.

Out of the 8 asparagine solutions, 7 showed a very distinct nitrification. One of the nitrified solutions, which had remained quite clear, was spread on gelatin; no growth was obtained. The calcium acetate appeared neither to facilitate nor retard the nitrification.

Of the 8 milk solutions, 5 showed distinct nitrification. One of these was clearly an impure culture; it became very turbid, a thick film formed on the surface, and it gave an abundant growth on gelatin. Three of the nitrifying cultures, which had remained without any increase of the natural turbidity of the milk, gave no growth on gelatin. The calcium acetate was apparently without influence.

Of the 8 urine solutions, 6 showed decided nitrification. One of these was contaminated with mould, but gave no growth of bacteria on gelatin. Two of the clear nitrifying solutions were spread on gelatin, and gave no growth. The calcium acetate exerted no beneficial influence.

Of the 8 urea solutions, only 3 have nitrified; one of these was tested on gelatin, and gave no growth.

These experiments should be regarded as preliminary only, as the course of nitrification has not been studied, or any quantitative experiments made. That the pure nitrous organism can attack nitrogenous organic bodies is, I think, fully proved. The nitrification observed has however been, especially in the case of asparagine and milk solutions, decidedly sluggish. The contaminated milk culture has nitrified to a much greater extent than the corresponding pure culture. It is quite possible, therefore, that other organisms may render considerable service in the process of nitrification, by making a preliminary attack upon organic matter.

FORM OF THE NITROUS ORGANISM.

The description of the nitrifying organism given by the French observers has been already noted (p. 496).

Frankland's description of the nitrous organism when grown in an ammonium chloride solution is as follows:—"The bacilli are about 0·8 μ in length, and hardly longer than broad, in fact their form is intermediate between that of a bacillus and micrococcus, so that the term bacillococcus may not inappropriately be used to designate them. They occur both isolated, in pairs, and in small irregular groups." Grown in broth, it forms "small bacilli, about 1·5 μ in length, and about 0·5 μ in breadth, sometimes, however, forming threads 5·7 μ in length in which the divisions are not generally apparent."

According to Winogradsky, the organism growing in an ammoniacal solution has generally the form of an elongated ellipsoid, but the youngest cells are nearly spherical. The breadth does not exceed 1·0 μ, the length is 1·1 — 1·8 μ. The longest are those about to divide, and exhibit a dumb-bell form. More rarely the organism is spindle-shaped with blunt ends. A chain of 3—4 individuals is very rare. When in repose the organism is united by a jelly, and loses all characteristic form. The organism has a temporary mobile stage of existence, during which the culture may become turbid.

Before mentioning the forms which have come under my own notice, I will say a word as to the mode of staining. The simplest, and one of the most satisfactory methods, when merely eye observations are desired, is to place a drop of the culture liquid on the glass slide, mix with it some filtered stain by means of a wire, place a cover-glass on the drop, and allow it to stand about half an hour; then press down the cover-glass, wipe off the liquid which exudes, and finally run Hollis' glue round the cover-glass. By this means the organism is stained in its own culture fluid; we see it in its true form, without any possible distortion of its shape by drying. The field is bright and clear, though coloured, for there has been no precipitation of matters during drying which are afterwards hard to remove.

When the preparation is to be mounted in balsam, a drop of the culture is dried in the centre of a cover-glass, which is then placed for some minutes in dilute acetic acid to remove matter which would cause turbidity. The cover-glass is then washed, dried, and stained for some hours in methyl-violet.

I have made no attempt to study the life-history of the nitrous organism, and the various forms which it assumes; my observations can only be regarded as furnishing material towards a more accurate knowledge of the subject; fortunately the excellent photographs executed by Mr. Pringle and Dr. Bousfield, which are appended, will give a more faithful representation of the organism than could be furnished by my own description.

The first form I have to mention consists of nearly spherical corpuscles, varying in size from mere points up to a diameter of 1·0 μ, which extreme limit is, however, rarely reached. This form is very striking, as it takes the stain deeply, and the extreme difference in size forms a remarkable picture. Occasionally the corpuscles of largest size are about to divide, and are seen as double organisms. This form is present in all cultures, and in some, as in milk and broth cultures 40 days old, was the only form observed. The minute point-like organisms certainly require explanation. They seem far too small to be produced by division of the full-sized organism.

The second form is the one generally described as the nitrifying organism. It is always longer than broad, and usually attains a length distinctly exceeding 1·0 μ. It appears frequently as a nearly regular oval. Sometimes it is egg-shaped, one end being larger than the other. Sometimes the ends are more or less truncated, and occasionally sharply so. Not unfrequently the form is much less regular. This phase of the organism takes the stain more feebly than the circular form; the more irregular and broken (?) it becomes, the more feebly is it stained.

One would naturally conclude with Winogradsky that the darkly staining circular forms were the young organisms; but, as already mentioned, a difficulty arises from the extreme minuteness of many of them.

I have seen nothing similar to Frankland's thread-forming bacillus, which he found in broth cultures.

The first pair of photographs show the nitrous organism as it appeared in an ammonium carbonate solution, and upon the cover glass sunk for 70 days in the same solution: this culture contained a few bacilli. Both photographs show the large elongated form of the organism, and on the sunk cover glass the maximum size is seen. The same large form of the organism occurs in ammonium sulphate solutions.

The second pair of photographs show the organism as found in weak broth, and in a $\frac{1}{2}$ per cent. milk solution. In both cases only the small circular form appears.

The magnification is in all cases 1000 diameters.

THE NUTRITION OF THE NITROUS ORGANISM.

1. *Independence of Organic Food.*—It has been hitherto held by vegetable physiologists that plants which are destitute of chlorophyll cells derive their carbon solely from organic matter, and are incapable of decomposing carbon dioxide. This doctrine apparently does not hold good in the case of the nitrifying organism, and possibly in that of some other bacteria.

It is curious that my first attempts at nitrification in solutions were made with no added organic matter, save the soil used as seed. Almost immediately, however, in obedience to the received opinion, I commenced the practice of including a neutral tartrate among the constituents of my solutions. The advantages attending the presence of this tartrate were not very apparent. In 1879, I say, "A proportion of organic carbon to nitrogen equal to 3 : 10 by weight is sufficient for the purposes of nitrification, and probably a smaller proportion of carbon would suffice." In the next report (Trans., 1884, **45**, 667), I compare the rate of nitrification in solutions containing 40 milligrams, and 160 milligrams of sodium potassium tartrate per litre. "The advantage as to speed of nitrification was in 7 instances with the larger proportion of tartrate, in 3 instances with the smaller, and in 5 instances the rate of nitrification was quite similar." With glucose instead of tartrate, in the proportion of 20, 50, 100, and 200 milligrams per litre, the advantage as to speed of nitrification was always with the smallest proportion of glucose.

In 1886 (Trans., **49**, 651), Dr. Munro raised the question—Is organic carbon essential to nitrification? He fully accepted the theory that organic matter is necessary for the nutrition of bacteria; he nevertheless records many experiments, made in the presence of mixed organisms, in which organic matter was plainly injurious to nitrification; and he has some experiments in which nitrification took place without any organic matter having been added to the solutions. He concludes that, "the merest traces of organic matter, such as may be furnished accidentally by occasional exposure to the dust of the air, are sufficient for complete nitrous fermentation of the quantities of ammonia used in these experiments."

After the publication of Dr. Munro's results, I made a few experiments with the view of ascertaining whether the presence or absence of a tartrate had any influence on the progress of nitrification. The experiments were devised so as to test at the same time how far the so-called "incubation period," preceding nitrification, could be diminished by carrying out to a fuller extent the plan I had previously described (Trans., 1884, 665), and with which Dr. Munro had been still more successful.

Three similar bottles each received 0·1 gram of soil, 100 c.c. of an ammoniacal solution, and some calcium carbonate. In bottle A, the solution merely contained 0·008 gram of ammonium chloride. In AM, there were, in addition, potassium phosphate, and magnesium sulphate. In AMT, the solution contained, in addition to the constituents in AM, sodium potassium tartrate, equal in weight to the ammonium chloride. The experiment commenced on July 8, 1886. As soon as any solution had nitrified it was decanted off, and 100 c.c. of a similar solution put in its place. The following table shows the comparative rapidity with which nitrification began, and the time occupied in oxidising the ammonia, in each solution:—

Interval before Nitrification commenced.

Solution.	1st culture.		2nd culture.		3rd culture.		4th culture.	
	Days before starting.	Order of starting.	Days before starting.	Order of starting.	Days before starting.	Order of starting.	Days before starting.	Order of starting.
A.......	22	3	about one	2	not one	3	not one	3
AM.....	13	2	"	1	"	1	"	1
AMT....	9	1	"	2	"	2	"	2

Duration of Nitrification (days).

A.......	22	22	23	50
AM.....	24	10	9	19
AMT....	22	19	11	28

The upper half of the table shows that when fresh ammoniacal solutions were placed in bottles in which nitrification had already occurred, the interval that elapsed before nitrification commenced suddenly diminished from many days to one, or less, a result perfectly accordant with that obtained by Dr. Munro. After the first culture, the solution AM, containing phosphates, &c., but no tartrate, was always the first to commence nitrification, but the difference between the three solutions is very trifling, amounting to only a few hours.

Again, after the first culture, the period of nitrification is always shortest in solution AM, and longest in A where ammonium chloride alone was present. The tartrate has here a distinctly retarding effect on nitrification. It should, however, be mentioned, that a larger proportion of nitrous acid, and less nitric, was found at the close of nitrification in AM than in AMT, so that the oxidation effected in the two solutions was more nearly alike than the figures would indicate. The great lengthening of the periods in the 4th culture is due to the commencement of winter temperature.

A shorter series of experiments was also conducted with similar solutions in which no soil was present, but the solutions were all seeded with 3 drops of a nitrified culture. The results again showed, though not in a marked manner, that nitrification commenced first where no tartrate was present. The most striking result was, however, obtained with the solution which contained the ammonium salt alone; here nitrification in each case began, but never proceeded to more than a small extent. The reason was doubtless the absence of phosphates, which I have already shown are essential for nitrification (Trans., 1884, **45**, 641).

In consequence of these results, I gave up the employment of tartrates as a constituent of ammoniacal solutions to be nitrified, and, as already mentioned, carried out a series of cultures in an inorganic solution when preparing for the isolation of the nitrifying organism. Professor P. F. Frankland has also employed an inorganic solution for the same purpose. His series of successive cultures is far longer than my own, and extends over more than two years; as, however, he employed cotton-wool stoppers, it is possible that organic matter might thus be introduced; my own experiments were made in stoppered bottles.

It is quite clear that the facts as yet stated do not amount to any proof that the growth and development of the nitrifying organism is independent of the presence of organic matter; no evidence has, in fact, been given that our solutions did not contain traces of organic matter, though none was intentionally added. To Winogradsky belongs the credit of establishing, in an unmistakable manner, the independence of the nitrifying organism of aid from organic matter.

Winogradsky ascertained, in the first place, that nitrification proceeded equally well when organic matter was rigorously excluded; he next determined, by a process of wet combustion, the amount of organic carbon produced from inorganic materials during nitrification; this portion of his work will be found in his second and third memoirs. He found the quantity of carbon assimilated during an energetic nitrification to be quite considerable. It appeared to bear a fairly constant relation to the amount of nitrogen oxidised, although the latter varied much in the experiments he quotes. For 1 of carbon assimilated, 35 4 of nitrogen as ammonia were, on an average, oxidised to nitrous acid. Winogradsky suggests that the first step in the formation of organic matter may be the construction of an amide from ammonium carbonate, and he reminds us that even the animal body is capable of effecting such a change, urea being in this case produced.

The doctrine that a vegetable cell destitute of chlorophyll, and growing in the dark, should be capable of constructing organic matter from an inorganic carbonate, presents quite as many difficulties to the chemist as to the physiologist, as the action in question is one requiring a considerable absorption of energy. The action becomes, however, perfectly possible, if we may take into account the energy liberated at the same time by the oxidation of ammonia. If the nutrition of the organism, and its oxidising effect on ammonium carbonate take place simultaneously, the formation of organic matter from carbonic acid will not be opposed to the teachings of thermochemistry;* as with an oxidation of 35 parts of nitrogen for an assimilation of 1 part of carbon, there is an abundant margin for an excess of heat development.

The energy produced by the oxidation of ammonia is not, of course, available as an explanation of the nutrition of the non-nitrifying organisms which accompany the nitrifying organisms in inorganic cultures. We must recollect, however, that under these circumstances the non-nitrifying organisms form, numerically, only a small minority of the total organisms present, and that we have little evidence of their capacity for growing alone in the absence of organic matter.

2. *Influence of Carbonates and Acetates on Nitrification.*—After the publication of Winogradsky's results respecting the assimilation of carbon from carbonates, I made a few experiments to ascertain whether the presence of soluble acid carbonates exerted any favourable influence on nitrification. In a previous paper (Trans., 1884, **45**, 653), I have shown that disodium carbonate, except when added

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* For a fuller discussion of the subject, I may refer to a paper by S. U. Pickering, F.R.S., published in *Nature*, 1890, **43**, 165.

in small proportion, hinders nitrification; while monosodium carbonate may be added in much larger quantity without harmful result.

Five wide-mouthed stoppered bottles were half filled with a solution containing 0·30 gram ammonium sulphate, 0·10 gram potassium phosphate, 0·07 gram magnesium sulphate, and a little calcium chloride per litre; some precipitated calcium carbonate was added to each bottle. After sterilising, bottle 2 had 24 bubbles of carbon dioxide passed through the solution. Bottle 3 received monosodium carbonate at the rate of 1 gram per litre. Bottle 4, disodium carbonate equivalent to the preceding Bottle 5, calcium acetate, 0 25 gram per litre. Bottle 1 had no addition. All were seeded with the pure nitrous organism from C3 on November 28, 1890. The bottles were kept at 22°.

Examined after 33 days, it was found that nitrification was completed in solutions 3 and 5, and was nearly completed in 2. Nitrification had commenced in 1, but was far from being completed. No nitrification whatever had occurred in 4. Examined again after 68 days, nitrification was completed in 1, but had not commenced in 4.

Thus with the pure nitrifying organism we find the same hindrance to nitrification from disodium carbonate which had been previously observed in impure cultures. The point, however, of chief interest is the advantage derived from passing carbonic acid, from the addition of monosodium carbonate, and from the use of calcium acetate.

In comparative experiments in which bacteria are the active agents, no definite conclusion should be drawn from one series of experiments, as it is impossible to introduce the same number of bacteria in each experiment, and the rapidity of the action depends much on the number of organisms present. The trial was therefore repeated.

Five bottles received an ammoniacal solution as before. After sterilising, about 10 c.c. of carbon dioxide were passed into bottle 1. Bottles 2, 3, and 4 received monosodium carbonate at the rate of 4, 6, and 8 grams per litre. Bottle 5 received calcium acetate at the rate of 0·5 gram per litre. In order to obtain accumulative effects, solution 1 was seeded from solution 2 of the previous series; solutions 2, 3, and 4 from solution 3; solution 5 from solution 5.

After 28 days, it was found that nitrification was completed in solution 5; it had made considerable progress in 2, less progress in 1, and had not commenced in 3 and 4. In 58 days, nitrification was completed in 1 and 2; it had commenced in 3, but not in 4.

The calcium acetate again appears as most favourable to nitrification; indeed, the nitrification in solution 5 is one of the most speedy I have noticed. The monosodium carbonate is also again superior to the carbonic acid, and it appears that as much as 4 grams per litre may be introduced without injury; 6 grams per litre was, however, plainly a great hindrance to nitrification, and with 8 grams no nitrification took place.

The beneficial effect which followed the addition of carbonic acid, or monosodium carbonate, may of course be regarded as possibly due to the increase of available base in the solutions; to the greater development, in fact, of a condition known to be essential to nitrification. I do not believe, however, that this is the true explanation of the facts, for the disodium carbonate, even in small quantity, was a hindrance and not a help; and in a similar series of experiments, to be presently mentioned, in which nitrites were converted into nitrates, the same beneficial action of monosodium carbonate was observed, although here a salifiable base took no part in the reaction. I am disposed, therefore, to regard the presence of an excess of carbonic acid in a nitrifying solution as exercising a beneficial influence by aiding the nutrition of the organism; it acts, of course, in combination with ammonia.

On the influence of calcium acetate a third experiment was made, using 0·25 gram per litre, and again the effect was distinctly to hasten nitrification. The calcium salt was employed in these experiments, because it permitted the destruction of the acetic acid without increasing the alkalinity of the solution.

The action of the acetate is certainly interesting. In the presence of the mixed organisms of soil, an acetate, according to Munro, hinders nitrification by favouring the development of organisms reducing nitrates; when the nitrifying organism alone has possession of the field, it certainly aids nitrification. There is no contradiction in the statement that the nitrifying organism can assimilate carbon both from inorganic and organic sources; the same is true of green plants, which, while they decompose carbon dioxide, can also be fed with sugar.

THE PRODUCTION OF NITRATES.

We have already seen that the nitrification which normally occurs in a mass of aërated soil results in the production of nitrates only; that a nitrification of the same kind may, under certain conditions, be conducted in an ammoniacal solution with either soil as the seed, or a solution recently nitrified with soil; but that if the attempt is made to make the action intensive by increasing the concentration of the solution, or raising the temperature, large quantities of nitrites are produced, which, after nitrification is completed, change often very suddenly into nitrates. We have seen, further, that by repeated cultivation in ammoniacal solutions the power of producing nitrates may be entirely lost, and that this change may be rapidly brought about if the culture liquids are made permanently alkaline with disodium carbonate, and especially if the soil at starting was taken from a pasture. Finally, the nitrifying organism which has been isolated after a series of cultures in ammoniacal solutions is only capable of oxidising ammonia to nitrite, and it is quite incapable of converting nitrites into nitrates.

It is clear from what has just been stated that the isolation of the nitrifying organism, as at present accomplished, does not solve the problem of nitrification; the production of nitrates has still to be accounted for. The question before us, in its simplest form, is clearly this:—Does soil contain *two* nitrifying organisms, one oxidising ammonia to nitrites, and the other oxidising nitrites to nitrates; or is there but one organism in soil, originally capable of oxidising ammonia to nitrates, but which has become enfeebled and lost a portion of its power during our processes of isolation?

It is well to recollect that the oxidation of ammonia to nitrite involves the consumption of three quarters of the oxygen necessary to form nitrates; the demand for oxygen thus falls chiefly on the production of nitrites, and but little on the formation of nitrates. Mr. Pickering has been good enough to calculate for me the quantity of heat set free in the two stages of the oxidation of ammonium carbonate; he finds that there is at least four times as much heat liberated during the formation of nitrite, as there is when nitrite is converted into nitrate. If these two operations are effected under similar conditions, and by a similar agency, we must, therefore, conclude that the production of nitrate is a much more difficult operation than the production of nitrite. This is undoubtedly a very important fact to bear in mind. It agrees well with the idea that the nitrite-producing organism, which has been isolated, owes its present character to degeneration; but it is no evidence against the supposition that there are two organisms.

1. *Earlier Rothamsted Work.*

I have now to give some account of my own work regarding the production of nitrates. The results of the earlier part of this work were obscure in their bearings, and led to no definite conclusions, they were therefore never brought before the Society. The real meaning of these observations has been made clear by the light of subsequent results. I now record them as a necessary introduction to the later work.

On September 27, 1879, experiments were started with the view of obtaining further information respecting the special properties possessed by certain cultures of producing nitrites or nitrates. Nine pint bottles received each 400 c.c. of a solution containing 0·08 gram ammonium chloride, 0·15 gram sodium potassium tartrate, 0·02 gram potassium phosphate, and 0·005 gram magnesium sulphate per litre, with calcium carbonate. The bottles were provided with cotton-wool stoppers. When sterilised, five bottles were seeded from cultures which had yielded only nitrites; three from cultures in which nitrates had been finally produced; while one received 0·5 gram of fresh soil. The quantity of nitrous acid formed in these solutions was determined each week with permanganate.

By the end of January all ammonia had disappeared in the eight solutions seeded from old cultures; in every case it appeared that nitrites only had been formed. In the solution seeded with soil, there was, on the other hand, a purely nitric oxidation.

The bottles were not looked at again till the following July (1880). In four bottles the surface of the solution was covered with small snow-white, floating masses, which when magnified appeared as a dense mass of interlacing hairs. In these four solutions the whole of the nitrous acid had disappeared, and nitric acid now existed. In the remaining solutions, the nitrites remained unchanged. One of the solutions still containing nitrites only was seeded with a little of the white organism from one of the other bottles: by September the organism had spread over the surface, and all nitrites had disappeared.

In order to test this action further, seven bottles were partly filled with a solution containing 1 gram of potassium nitrite, 0·25 gram sodium potassium tartrate, 0·05 gram potassium phosphate, and 0·01 gram magnesium sulphate per litre; some calcium carbonate was added. Two of these bottles were seeded on July 14, 1880, with the white surface organism; two with pasture and arable soil respectively; two with a nitrified solution which had produced only nitrites; one was unseeded. On August 26, no diminution in the nitrite had taken place in any case. On September 24 the nitrite had disappeared in the two solutions seeded with the white organism, which had now grown over the whole surface. The nitrite had also disappeared in the solution seeded with arable soil. The remainder of the solutions were unaltered. On February 24, nitrites were no longer present in the solution seeded with pasture soil. None of the other solutions had altered when examined two years afterwards. There appeared thus to be presumptive evidence of a connection between the growth of the white surface organism and the conversion of nitrites into nitrates.

The white surface organism was microscopically examined by Dr. M. T. Masters, and more fully by Professor E. R. Lankester; both of them pronounced it to be a bacillus. It occurs as a network of branched filaments, which in older specimens are apparently charged with spores throughout their whole length. At the outer edge of the network, groups of cocci are generally present.

The next experiments with the surface organism gave important results: the primary object in view was to ascertain whether the organism would nitrify ammonia. Four experiments were made with the usual ammoniacal solution, containing 0·08 gram ammonium chloride, a tartrate, phosphate, &c.; and two experiments with a urine solution (4 c.c. per litre). In each group half the experiments were made at 30°, and half at the temperature of the air. One of the ammoniacal solutions was seeded with the surface organism from one of the original ammoniacal cultures of September 27, 1879; the other five solutions were seeded from the sub-cultures in potassium nitrite just described. As nitrification of ammonia had actively taken place in the cultures of September, 1879, it was probable that in transferring the surface organism some of the nitrifying organism would be transferred with it. In the solution seeded from the ammoniacal culture, the nitrification of the ammonia was completed in two months, first nitrous and then nitric acid being formed. Out of the five ammoniacal solutions seeded from the nitrite cultures, one solution nitrified, the remaining four did not. In those four cases, powdered pumice, freshly ignited, was thrown into the bottles after the organism had spread over the surface, with the object of sinking a portion of it; this operation, however, did not effect nitrification. To each of the four bottles 0·10 gram of potassium nitrite was then added. In about one month's time (less at 30°, longer in the cold) the whole of the nitrite had disappeared, while the amount of ammonia, as shown by the tint given by Nessler's reagent, remained unchanged. We were thus apparently dealing with an agent *which could not oxidise ammonia, but which was energetic in converting nitrites into nitrates.* The one failure among the five solutions would probably be due to the fact that a single culture in a nitrite solution was insufficient wholly to remove the organism which oxidises ammonia.

At the Meeting of the British Association in September, 1881, I exhibited the white surface organism; and with a good deal of reserve mentioned the principal facts now stated. I then thought it possible that the surface organism was a phase in the life history of the nitrifying organism.

In the numerous nitrification cultures made since this date in perfectly similar solutions, the appearance of this white surface growth has been rare, and has been confined to cases in which fresh soil had been used as seed. I have found apparently the same organism on the surface of rain-water stored in the laboratory. It is quite possible that the organism originally entered the solutions as an air contamination (though this was not the view taken of the matter at first), the original bottles being opened every week for the determination of nitrous acid. The work at that time was also carried out in the general laboratory, and not in the private room afterwards used. It is quite certain that the occurrence of a surface growth is not essential for the conversion of nitrites into nitrates, as this has taken place in a multitude of cases without any such appearance.

The white surface organism was taken to the Brown Institution in 1886, where I went to learn the modern methods for separating organisms. The result of a hasty cultivation on gelatin was the isolation of a bacillus which I have called *B. sulphureus* (Trans., 1888, **53**, 730). This, however, was found to have no effect either on ammoniacal or on nitrite solutions.

2. *Recent Rothamsted Work.*

The subject of the production of nitrates acquired a new importance when it appeared that the nitrifying organism isolated by Frankland produced nitrites only. It was clear that half of the question still remained to be solved. In May, 1890, I therefore returned to the subject, and proceeded to operate with those cultures of the white surface organism which were not dried up.

By culture on potato four very distinct bacilli, and a penicillium were easily isolated. None of these organisms was, however, the actual white surface growth, but simply impurities associated with it. The white organism is of slow growth; the potato was rapidly overrun with the organisms just mentioned. All these organisms, and mixtures of them, were sown in ammoniacal and in nitrite solutions, but without result.

At the same time that the potato cultures were started, some of the white surface organism was sown on a nitrite solution, containing as before a tartrate, phosphate, &c. The organism slowly grew over the surface, but no disappearance of the nitrite took place. As it was quite certain that an agent capable of converting nitrites into nitrates had been originally present in the earlier cultures, the three bottles still containing fluid were well shaken, and a large seeding (12 drops) from each was added on July 15 to sterilised solutions containing 0·30 gram potassium nitrite, 0·15 gram sodium potassium tartrate, 0·05 gram potassium phosphate, 0·025 gram magnesium sulphate, and 1 c.c. of urine per litre, with some calcium carbonate. The bottles were kept at 22°. The white organism very slowly spread over the surface of all three cultures. In one of them the nitrites entirely disappeared, in the other two the nitrites remained, notwithstanding the presence of the white organism. There were thus three instances of the development of the white organism in a nitrite solution without any oxidation of the nitrite following, and it became evident that the white organism was not the agent producing nitrates, but some other associated with it.

Nutrition of the Nitric Organism.

I had now (October, 1890) a solution capable of converting nitrites into nitrates. Before making any further attempt to isolate the active organism, some experiments were made to ascertain, if possible, what were the conditions most favourable to the production of nitrates. A series of eight stoppered bottles was prepared. All were half filled with a solution containing 0·3 gram potassium nitrite, 0·10 gram potassium phosphate, and 0·05 gram magnesium sulphate per litre, with some calcium carbonate.*—1 contained this solution alone; 1*b*, the same *plus* monosodium carbonate, 1 gram per litre. 2, the nitrite solution *plus* ammonium sulphate, 0·033 gram per litre; 2*b*, the same *plus* monosodium carbonate as above. 3, the nitrite solution *plus* sodium potassium tartrate, 0·20 gram per litre; 3*b*, the same *plus* monosodium carbonate. 4, the nitrite solution with calcium acetate, 0 25 gram per litre; 4*b*, the same, *plus* monosodium carbonate. The monosodium carbonate and the ammonium sulphate were added after sterilisation. The monosodium carbonate was added with the object of supplying carbonaceous food; it was used in these experiments before its use in the nitrifying cultures already described (p. 512). The solutions were all seeded on October 11 from the solution already mentioned, in which nitrites had recently changed to nitrates. The bottles were kept at 22°.

On November 22, the nitrite had entirely disappeared in 1*b*, 2*b*, 3*b*, 4, and 4*b*; it had diminished in 1, and was apparently unchanged in 2 and 3. At this date there was no appearance of a white surface growth on solution 1*b*, and very little appearance of it on the other solutions in which the nitrite had disappeared. Afterwards the surface growth developed on all the solutions. In the subcultures afterwards described no surface growth has as yet appeared.

On December 31, the nitrite had disappeared in 1 and 3, but remained unaltered in 2. On February 10, the nitrite in 2 was still unchanged.

These experiments threw new light on the subject. It was clear that the change from nitrite to nitrate could be readily effected in the absence of any added organic matter. The tartrate had apparently no beneficial influence, but the acetate apparently had. The presence of monosodium carbonate was clearly an advantage, the change taking place more speedily for its presence in three cases out of four. The ammonium salt had apparently a prejudicial action save where monosodium carbonate was present, in which case the ammonia was removed by nitrification.*

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* The addition of calcium carbonate has been continued throughout these experiments, although no base is needed for the conversion of nitrite into nitrate. It served to supply lime, which could not be added as a soluble salt without impairing the clearness of the solution.

To examine still further the influence of monosodium carbonate, calcium acetate, &c., a series of five bottles was started—1 contained the nitrite solution alone, with calcium carbonate. 2, the same, with carbonic acid passed into the solution. 3, nitrite, *plus* monosodium carbonate, 1 gram per litre. 4, nitrite, *plus* monosodium carbonate, 4 grams per litre. 5, nitrite, *plus* calcium acetate, 0·25 gram per litre. On November 29, all the solutions were seeded from 1*b* in the previous series.

On January 1, 1891, the nitrite was found to have disappeared in 2, 3, and 4; in 1 and 5 there was little if any change in its amount. On February 4, the nitrite had disappeared in 1, but not in 5. On April 1, the nitrite had disappeared in 5.

We have here a favourable influence exerted by carbonic acid, and by monosodium carbonate; of the latter, 4 grams per litre is not, apparently, an excessive proportion. The acetate in this series has apparently a retarding influence.

A further series of five bottles was started on January 7, 1891.—1 contained the nitrite solution and calcium carbonate, *plus* carbonic acid; 2, the nitrite *plus* monosodium carbonate, 4 grams per litre; 3, the same, with 6 grams per litre; 4, the same, with 8 grams per litre; 5, the nitrite with calcium acetate, 0·25 gram per litre. Solutions 1 and 5 were seeded from 2; solutions 2, 3, and 4 from 4 in the previous series.

On February 4, the nitrite had distinctly diminished in 1, but not in the others. On March 6, the nitrite had entirely disappeared in 1, 2, 3, and 5, but was unchanged in 4. On April 7, the nitrite was still unchanged in 4.

The carbonic acid is here again favourable to the production of nitrates. Of the monosodium carbonate, 6 grams per litre were successfully employed, though with a somewhat less speedy action than when 4 grams were used. 8 grams are, however, too much, and no change has taken place with this addition. The acetate here gives a good result, but inferior to that given by carbonic acid.

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* The ammonium in 2*b* nitrified to nitrate; it did not in 2. The nitrite culture from which all these solutions were seeded was itself seeded from the old ammoniacal culture of 1881, which had nitrified (p. 517). The nitrous organism was thus probably present in small quantity. It soon disappeared in the subsequent cultivations in nitrite solutions.

One more series of four solutions with carbonate and acetate has to be recorded.—1 contained with the nitrite 2 grams of monosodium carbonate per litre. 2, an equivalent quantity of disodium carbonate. 3, calcium acetate, 0·25 gram per litre. 4, the same, 0·5 gram per litre. The solutions were all seeded on February 27 from bottle 2 of the November 29 series.

On March 10, the nitrites had disappeared in solution 1, but not in the others. On March 26, no change having occurred in 2, 3, and 4, they were all reseeded from 1. On April 27, the nitrite had disappeared in 3. On May 13, the nitrite had begun to diminish in 4, but remained unchanged in 2.

We have here evidence, as in the experiments with the nitrous organism, that disodium carbonate acts very prejudicially on the reaction. The smaller quantity of acetate is again less favourable than the supercarbonate, and the larger quantity is apparently prejudicial.

The nutrition of the nitric organism thus apparently proceeds on the same lines as that of the nitrous; like it, it flourishes in inorganic solutions, and is considerably aided by the presence of supercarbonates. The nutrition of the nitric organism presents no real difficulty to the thermic chemist if only the proportion of nitrite oxidised bears a sufficiently high relation to the proportion of carbon assimilated from carbonates. Thus, according to Mr. Pickering's calculation, cellulose might be formed with the evolution of heat if 9 parts by weight of nitrogen as nitrite were oxidised for 1 part of carbon assimilated, a relation much narrower than that observed by Winogradsky in the case of the nitrous organism.

Behaviour of the Nitric Organism with Ammonia.

A solution containing 0·20 gram ammonium chloride, 0·10 gram ammonium sulphate, 0·10 gram potassium phosphate, 0·10 gram magnesium sulphate per litre, with calcium carbonate, was placed in three bottles. 1 received carbonic acid gas; 2, monosodium carbonate, 1 gram per litre; 3, calcium acetate, 0·25 gram per litre. All were seeded on January 7, 1891, from bottle 4 of November 29, and kept at 22°.

No nitrification had occurred in any case on April 3 (86 days). The solutions were then all reseeded from bottle 1 of the January 7 series (p. 520). Examined again on May 30 (57 days after the second seeding), it was again found that no nitrification had occurred.

A similar ammoniacal solution, containing 0·25 gram calcium acetate per litre, and calcium carbonate, was used for the three following experiments. The calcium acetate was added because it had been found so favourable to nitrification in other experiments. One bottle was seeded on March 11 from bottle 1, January 7. Two bottles were seeded on April 3, one from bottle B1, the other from B4, in the dilution-method series to be presently mentioned. All were kept at 22°. Examined on May 30, at 80 and 57 days respectively after seeding, no nitrification was found to have taken place in any instance.

These results are very remarkable; they entirely confirm the earlier results obtained in 1881 with cultures far more impure (p. 517). Nothing can more distinctly mark the wide difference between the nitrous and nitric organism than the fact that the first readily oxidises ammonia, and the second cannot. Further experiments were made to see whether the presence of ammonia was any hindrance to the action of the nitric organism upon nitrites; these trials were suggested by the apparently prejudicial influence of ammonia in experiment 2, October, 1890 (p. 519). The nitrite solution employed contained 2 grams of monosodium carbonate per litre. Two bottles contained the solution without addition; in two others, 0·2 gram of ammonium chloride per litre had been dissolved in the solution. One bottle in each series was seeded on April 2 from B1, and the remaining pair from B4 (see p. 523). On April 27 (25 days), the nitrite had all disappeared in the two solutions without ammonia, but remained practically unchanged in quantity where ammonia had been added. The solutions were re-examined on May 30; the nitrites still remained undiminished where ammonia was present; the ammonia also was apparently undiminished.

The fact that the presence of ammonium carbonate hinders the development of the nitric organism has already appeared in other experiments. We have indeed become familiar with the fact that cultivations in a solution of ammonium carbonate constitute the most effective method for the elimination of the nitric organism.

Attempts to Isolate the Nitric Organism.

The earlier examinations of the organisms separated on gelatin and on potato have been already mentioned (p. 518).

On January 2, solutions 2, 3, and 4 of the November 29 series were spread on gelatin; all gave abundant growths. The growth from solution 2 was non-liquefying and apparently pure, all the colonies being alike. The growths from the other cultures liquefied. A plate culture was then made from solution 2; again there seemed to be but one organism present, a small, stout bacillus. Four nitrite solutions, containing 1·0 gram monosodium carbonate per litre, were seeded on January 23 from various colonies. No diminution of the nitrite has been perceived in these solutions.

On January 12, an attempt was made to isolate the nitric organism by the dilution-method. Fifteen stoppered bottles were half filled with a solution containing potassium nitrite, 0·50 gram; potassium phosphate, 0·10 gram; magnesium sulphate, 0·10 gram; monosodium carbonate, 1·0 gram per litre, with calcium carbonate. Each bottle had carbonic acid passed into the solution before sterilising. The culture used as seed was solution 2, November 29. Bottles A1—3 were seeded with a 1/1000 dilution; B1—4, with a 1/10,000 dilution; C1—4, with a 1/100,000 dilution; D1—4, with a 1/1,000,000 dilution. The bottles were kept at 22°.

On March 9 (56 days), the nitrite was found to have disappeared in A2, A3, and B1. On March 23, it had disappeared in A1, B2, B3, B4. The remaining solutions have since been frequently examined, but no further change has occurred. Thus, all the solutions seeded with the 1/1000 and 1/10,000 dilutions have given evidence of the presence of the nitric organism, but no others. This result was not hopeful. It was soon found that all the active solutions gave growths on gelatin. A2 and A3 contained clearly two organisms. B1 gave an apparently pure culture, slowly liquefying. In the liquefied gelatin, the organism formed a pale yellow deposit. When stained, it appeared to be the small, stout bacillus previously obtained from the solution employed as seed. B2 and B3 gave growths which slowly liquefied; the growth from B4 showed no liquefaction. As B1 and B4 had apparently the best claim to be considered pure, subcultures were prepared from single colonies of the growths on gelatin, and from these subcultures nitrite solutions were seeded on April 13. No diminution in the nitrite in these solutions has been observed.

The attempts to isolate the organism thus failed. It is presumably, from the evidence before us, one that will not grow on gelatin.

Microscopic examinations were made of several cultures of the nitric organism. In the purer cultures the associated bacilli growing on gelatin were few in number, and it was not difficult to obtain fields in which they were absent. Such a field, from the culture B4, has been photographed, and will be found at the end of this paper. The organism is seen to consist of circular corpuscles of very different size, quite similar to what has been already described as one of the forms of the nitrous organism.

THE THEORY OF NITRIFICATION.

The time at my disposal has not allowed any complete study of the origin or properties of the nitric organism; only a few of its salient properties have been pointed out. It may be said that I have not even satisfactorily proved that the organism I have experimented with was derived from soil, though of this there can be little doubt. With the experience now gained, it may be pretty safely predicted that if a series of cultures be made in an inorganic nitrite solution, such as I have employed, starting with soil as the seed for the first culture, a point will soon be reached at which only the property of converting nitrites into nitrates will be retained, while the power of oxidising ammonia will be lost. Such a process would run parallel with that already established for the separation of the nitrous organism; here a series of successive cultures in solutions of ammonium carbonate determines a loss of all power to oxidise nitrites, while the power of oxidising ammonia to nitrites remains.

Does soil contain both a nitrous and a nitric organism: or does the original organism embrace both properties, and lose a part of its power when cultivated in unsuitable media? The cultivations on gelatinous silica, which Winogradsky has initiated, will supply the most decisive answer to this question, for this method will allow of the separation of the organisms directly from the soil, and the testing of their powers without their previous cultivation for many months in a liquid medium. The evidence at present, however, seems to point very clearly to the existence of two organisms of very different properties, but belonging to the same class.

In support of this view, we may remark that there is no apparent reason why the power of oxidising nitrites should be lost during the process for obtaining the nitrous organism, as in every culture in ammonium carbonate nitrites are produced, and an opportunity given for the exercise of the function possessed by the nitric organism. The reason why successive cultivations in ammonium carbonate finally eliminate the nitric organism is apparently to be found in the hindrance to its development presented both by ammonia and by an alkaline condition of the solution,* unless the alkali is present as a supercarbonate of calcium or sodium.

There is perhaps more reason for assuming that the power of oxidising ammonia may be lost during successive cultivations in liquids in which ammonia is absent; but the loss of this power occurs so speedily, that it is more natural to assume that the nitrous organism fails to grow when ammonia is absent.

The facts observed during the nitrification of ammoniacal solutions by soil also point to the existence of two agents. A purely nitric nitrification occurs, we have seen, only when the ammoniacal solution is weak. When the solution is stronger, much nitrous acid is at first produced; indeed, when a small quantity of soil has been added, it is quite frequent that nearly the whole of the ammonia should be converted into nitrite before the production of nitrate begins. Frequently, too, there is a long pause after the oxidation of ammonia to nitrite before the oxidation to nitrate commences. This pause is probably a true incubation period, the nitric organism not beginning to develop till the ammonia had greatly diminished or disappeared.

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* If the latter part of this explanation is true, the development of the nitric organism in an ammonium chloride solution should be more injured by the addition of disodium carbonate than is the case with the nitrous organism. This has not yet been made the subject of experiment.

We may here remark that in a soil the conditions are quite different from those occurring in one of these cultures. The nitric organism is there present at starting in large quantity, and is not required to develop under adverse circumstances. Moreover, the proportion of ammonia present at any time is extremely small, and the alkali is always a supercarbonate.

The actual dislike of the nitric organism for ammonia, and the fact that it cannot oxidise it, are points of difference from the nitrous organism so great that it is difficult to believe that they are merely the result of successive cultivations in a solution containing nitrites in place of ammonia.

The points of similarity between the nitrous and nitric agents are also numerous. Both belong to a class flourishing in inorganic solutions. Both are aided in their work, probably in their nutrition, by the presence of supercarbonates. The agreement in their attitude towards acetates is not so certain, the nitrous organism being apparently more benefited than the nitric. The development of both is greatly hindered or prevented by the presence of neutral alkali carbonates. Neither of them apparently will grow on gelatin. Lastly, the form of the two organisms is, apparently, similar. It is hazardous to make such an assertion before the nitric organism has been satisfactorily isolated; but as the cultures which convert nitrites into nitrates, and fail to oxidise ammonia, are full of small, round cocci, which appear perfectly to resemble those which occur in the pure cultures of the nitrous organism, it is at present difficult to escape from such a conclusion.

A further study of the nitric organism should be of great interest. What is its action upon organic matter? Is this, or the nitrous organism, the agent in the conversion of iodides into iodates, and bromides into bromates, which Müntz has shown to be accomplished by soil? These and other questions belonging to this interesting subject I must now leave to others.*

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* Since writing this paper I have seen the communication made by Müntz to the French Academy on May 19, on the production of nitrates in soil. He now

I must not close this paper without expressing my great indebtedness to Dr. E. Klein, F.R.S., for the cordial assistance and advice he has at all times given me in the bacteriological work: without this advice I should many times have gone astray.

SUMMARY OF RESULTS.

1. The nitrification occurring in a mass of aërated soil, or produced by seeding with soil a cold, weak, ammoniacal solution, is purely nitric in character. If the ammoniacal solution is strong, or the temperature raised, a large quantity of nitrous acid is produced, which is finally converted into nitric acid. Soil readily converts a solution of nitrite into nitrate.

2. Pasture soil produces nitrites more readily than arable soil.

3. A clay subsoil, down to 4 feet from the surface, was found to produce nitrates.

4. In 1878 ammoniacal cultures were obtained (a third or

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regards the work of the nitrifying organism as confined to the oxidation of nitrogenous matter to nitrites, and believes that the conversion of nitrite into nitrate is not the work of an organism, but is brought about by the joint action of carbonic acid and oxygen. He states that in a weak solution of calcium nitrite the joint action of carbonic acid and air determines a conversion into calcium nitrate.

Whether or not the conversion of nitrite into nitrate in soil can possibly take place by a simple chemical reaction such as Müntz has described, it is quite evident that such a theory is incapable of accounting for the facts I have narrated in the present paper.

1. We have seen that the production of nitrites only, or of nitrates, in an ammoniacal solution, can be determined by the character of the culture with which the solution is seeded.

2. We have abundant evidence that in a solution of potassium nitrite conversion into nitrate can be determined by the introduction of the "nitric organism."

I have not enumerated in my paper the many blank experiments which formed part of the various trials; it has been stated, however, that in the attempt to isolate the nitric organism by the dilution-method, no change occurred in eight of the nitrite solutions, a sufficient proof that no spontaneous conversion of nitrite to nitrate took place.

The action of carbonic acid upon my potassium nitrite solution was made the subject of experiment before this gas was employed in the trials I have described. Before commencing the cultures of November 29, a current of carbonic acid was passed for about an hour through some of the nitrite solution about to be employed; to this solution a little of Trommsdorf's reagent (zinc iodide and starch) had previously been added. No blue coloration appeared; and it was consequently concluded that no nitrous acid had been set free.

I have not tried the action of carbonic acid upon calcium nitrite. This salt has been produced in all cases in which ammonia has been oxidised by the nitrous organism in the presence of calcium carbonate. Calcium nitrite solutions thus produced are quite permanent. I have in two cases added the nitric organism to such cultures, and succeeded in turning the nitrite into nitrate.

fourth from one seeded with soil), yielding only nitrites, which remained permanent. Subsequently other cultures were in the same condition.

5. Such nitrous cultures produce nitrites alone in solutions of ammonia, asparagine, urine, and milk. Their action is not altered by cultivation in shallow liquids with abundant aëration, or by a temperature of 30°.

6. It is difficult to prove that no trace of nitric acid is produced by this nitrous agent, from the want of a sufficiently good analytical method. If a small quantity of nitrate is formed it must be as a bye-product, as the nitrous agent does not oxidise nitrites.

7. It was at first thought that the age of the culture was the factor which determined the loss of the power of producing nitrates, but this idea was negatived by subsequent experiments. Successive cultivations in an alkaline solution (as ammonium carbonate) were found to be a certain method of obtaining the purely nitrous agent.

8. The production of nitrites by the above-mentioned agent is not due to a process of reduction; it readily takes place in inorganic ammoniacal solutions.

9. After the nitrification of an ammoniacal solution, if not too weak, gelatinous flocks frequently appear at the bottom of the vessel. If precipitated calcium carbonate has been introduced, it assumes a curdled appearance, and when treated with acid the gelatinous matter is left. When highly magnified, the jelly is seen to consist of highly refractive, circular corpuscles.

10. A large number of organisms, from many sources, obtained as pure cultures on gelatin, were introduced into ammoniacal solutions, but no nitrification was in any case obtained.

11. Successive cultivations, the first seeded with soil, were made in an inorganic ammonium carbonate solution, supplied with phosphates, &c.; the product became wholly nitrous at the second culture.

12. The organisms seen in these ammonium carbonate cultures were chiefly cocci, oval or round, the latter the smaller, and staining most deeply.

13. When such ammoniacal cultures were spread on gelatin, or on agar-agar, no such cocci appeared, although the composition of these media had been specially contrived to agree with that of well-known nitrifiable solutions. From several of the ammoniacal cultures only a single species of bacillus was obtained by cultivation upon gelatin or agar-agar.

14. None of the growths obtained on gelatin from nitrified solutions were found to produce nitrification when introduced into suitable liquid media, nor when placed on marble moistened with an ammoniacal solution.

15. Broth, and broth with solution of ammonium carbonate, were seeded with the nitrified cultures, and examined microscopically. The bacilli present in the cultures used as seeds were greatly developed in the broth; besides these, only small, dark points were seen in the stained preparations. The mixture of broth and ammonium carbonate readily nitrified.

16. Three series of trials to separate the nitrifying organism by the dilution-method failed; a fourth, in which an ammonium chloride solution with calcium carbonate was the culture liquid, succeeded. Out of 20 solutions, 10 nitrified, and of these 3 gave no growth on gelatin.

17. The organism thus separated oxidises ammonia to nitrous acid only; it is, in fact, the nitrous agent studied in my earlier experiments. Solutions of a nitrite seeded with this organism do not yield nitrate.

18. The nitrous organism grown in broth containing calcium nitrate did not reduce the nitrate to nitrite.

19. The nitrous organism does not grow on gelatin, or on agar-agar. It grows slowly in weak broth, but without impairing its transparency, or producing any other visible change.

20. The pure nitrous organism is capable of producing nitrous acid in solutions of asparagine, milk, urine, and urea; the last mentioned was apparently the most difficult to attack. The nitrification of the milk and asparagine made slow progress. All the cultivations of the pure organism were free from turbidity.

21. The nitrous organism occurs as nearly circular corpuscles, varying from minute points up to nearly 1·0 μ in diameter, sometimes double when division is approaching; these circular organisms stain deeply. It may also occur as oval cocci, the lengths frequently exceeding 1·0 μ, and the ends not unfrequently more or less truncated. There may also occur very irregular and broken (?) forms which take stain but feebly.

22. When the mixed organisms of soil are present in an ammoniacal solution, nitrification is hindered by the presence of a tartrate.

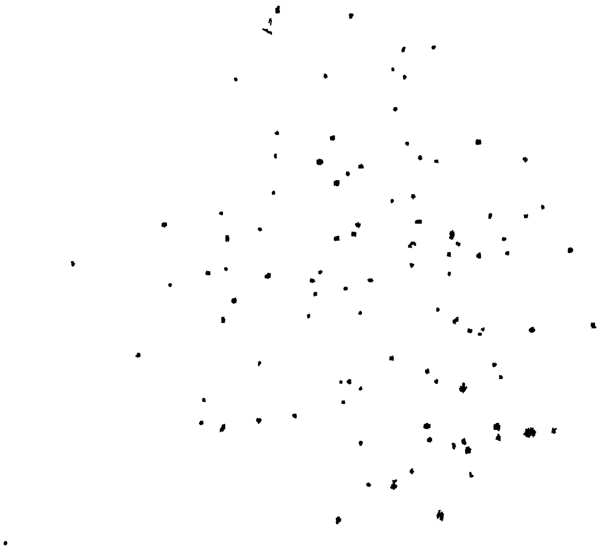
23. The nitrous organism will readily develop, and oxidise ammonia to nitrous acid, for apparently an unlimited number of successive generations in solutions to which no organic matter has been added, but phosphates are essential for this development. Winogradsky has supplied quantitative proof that the organism produces organic matter from inorganic materials, and finds on an average about 35 parts of nitrogen oxidised for 1 part of carbon assimilated from ammonium carbonate. The energy developed by the oxidation supplies apparently an explanation of this otherwise improbable reaction.

NITROUS ORGANISM × 1000.

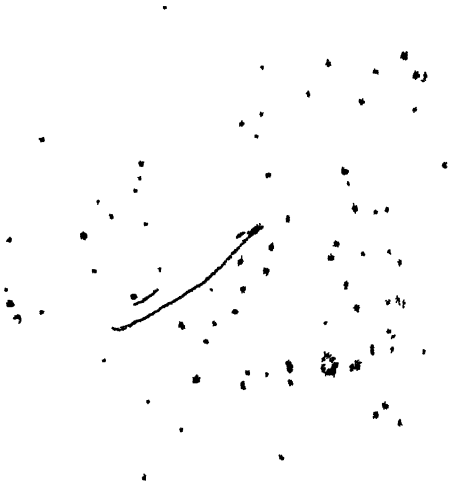
IN AMMONIUM CARBONATE SOLUTION.

SUNK COVER-GLASS
IN AMMONIUM CARBONATE SOLUTION.

NITROUS ORGANISM × 1000.



IN BEEF BROTH AT 22°.



IN HALF PER CENT. MILK AT 22°.

NITRIC ORGANISM × 1000

IN POTASSIUM NITRITE SOLUTION

24. In pure cultures of the nitrous organism in ammoniacal solutions, the addition of carbonic acid, monosodium carbonate, or calcium acetate facilitates nitrification, the addition probably supplying carbonaceous food. Disodium carbonate greatly hinders nitrification.

25. Results obtained in 1880—81 revealed the existence of an organism which energetically converted nitrites into nitrates, but was apparently unable to oxidise ammonia.

26. In 1886 and 1890, attempts were made to separate the active organism from the 1881 cultures by growth on gelatin and potato; none of the organisms thus separated had any power of oxidising ammonia or nitrites.

27. Recent results show that the nitric organism develops in inorganic solutions, and energetically converts nitrites into nitrates, especially if supercarbonates are present. Monosodium carbonate, 1—4 grams per litre, exerted a favourable influence, 6 grams a retarding influence. Disodium carbonate greatly hinders its action.

28. The nitric organism produces neither nitrites nor nitrates in ammoniacal solutions, even when carbonic acid, or monosodium carbonate, or calcium acetate is supplied.

29. The presence of ammonia is apparently a hindrance to the action of the nitric organism on nitrites, even when monosodium carbonate is present.

30. The dislike of the nitric organism for ammonia explains the course of nitrification when comparatively strong solutions of ammonium salt (1 gram per litre) are seeded with a small quantity of soil; much nitrous acid is then produced, and the formation of nitric acid sets in only when the ammonia has greatly diminished in quantity.

31. An attempt to isolate the nitric organism by the dilution-method failed, but apparently only one other organism, a stout bacillus, growing on gelatin, was present in some of the cultures. The stained preparations from these cultures contained an abundance of the minute circular organisms observed in pure cultures of the nitrous organism; the form of the two organisms is thus apparently similar.

32. The nitrification effected by soil is thus explained as performed by two organisms, one of which oxidises ammonia to nitrites, while the other oxidises nitrites to nitrates. The first organism is easily separated from the second by successive cultivations in solution of ammonium carbonate. The second is (probably) separated as easily from the first by successive cultivations in solution of potassium nitrite containing monosodium carbonate.

33. In soil, the nitric organism is equally active as the nitrous, since soil never contains any but extremely weak solutions of ammonia, and supercarbonates are always present.

XLVIII.—*The Iodometric Estimation of Nitric Acid in Nitrates.*

By George McGowan, PhD.

While working out the following method, the author was under the impression that it was new; but, after it had been communicated to the Chemical Society, under the title, "A New Method for the Estimation of Nitric Acid in Nitrates," he found that a paper by L. L. De Koninck and A. Nihoul had been published in the *Zeitschrift für angewandte Chemie*, August 15, 1890, giving details of a process depending upon the same principle. The priority of the idea, therefore, belongs to Messrs. De Koninck and Nihoul. The details of the method and the apparatus employed are, however, very different in the two cases.

When a fairly concentrated solution of a nitrate is warmed with an excess of pure, strong hydrochloric acid, the nitrate is completely decomposed, and the production of nitrosyl chloride and chlorine is *quantitative*, the reaction, as Tilden has shown (*J. Chem. Soc.*, 1874, **27**, 630; and Trans., 1885, **47**, 86), being as follows:—

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

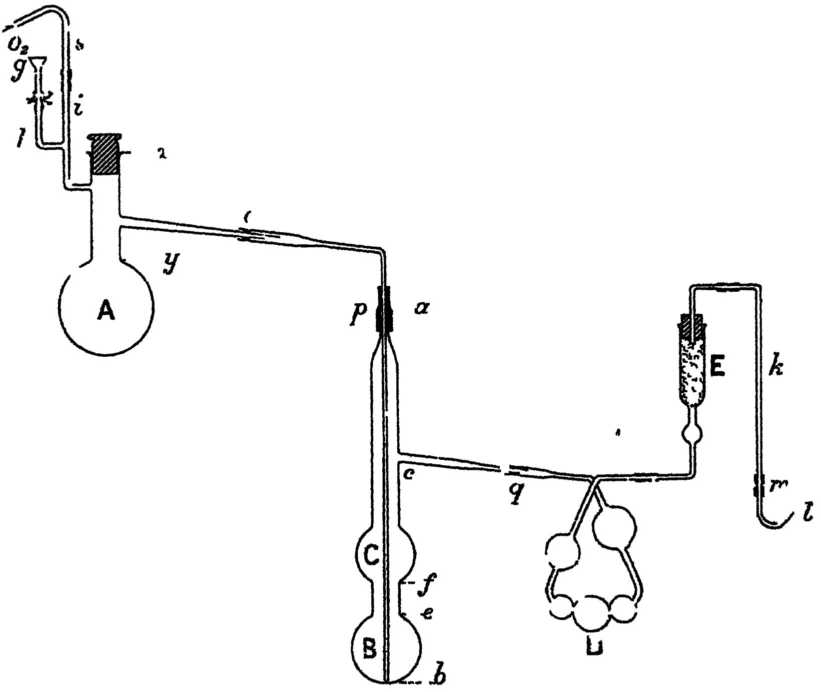
If the operation is conducted in an atmosphere of carbonic acid, and the escaping gases are passed through a solution of iodide of potassium, an amount of iodine is liberated exactly equivalent to the *whole* of the chlorine present (free and combined), nitric oxide escaping. 1 mol. of nitric acid thus yields 3 atoms of chlorine or iodine. The iodine can then be titrated in the usual manner with sodium thiosulphate.

It is, of course, absolutely essential for this process that air should be completely excluded from the apparatus, as, if any were present, the escaping nitric oxide would be re-oxidised to nitrogen trioxide or tetroxide, and this would in its turn liberate a further quantity of iodine from the iodide solution.

The apparatus required is very simple, and can readily be made by any one moderately expert at glass-blowing. The main point to be attended to is to have no corks or rubber stoppers, &c., for the escaping chlorine to act upon. Fig. 1 is a sketch of the apparatus; the condensing arrangement for the chlorine does its work perfectly, and may therefore be used with advantage, not only for this, but also for other similar methods in which iodine is set free. The measurements given are those of the apparatus as used by myself, which has proved of a very convenient size.

A is a small, round-bottomed flask, into the neck of which a glass stopper, *x*, is accurately ground (with fine emery and oil). The capacity of the bulb is about 46 c.c, and the length of the neck, from *x* to *y*, 90 mm. The first condenser is a simple tube, slightly enlarged

FIG. 1.



at the foot into two small bulbs (compare Sutton's *Volumetric Analysis*, 4th edition, p. 103). The length from *a* to *b* is 300 mm., from *b* to *c* 180 mm., and from *e* to *f* 30 mm. The capacity of the bulb *B* is 25 c.c., and the total capacity of the two bulbs and tube, up to the top of *C*, 41 c.c. This condenser is immersed, up to the level of *c*, in a beaker, full of water. *D* is a Geissler bulb apparatus (Dittmar's modification was used), and *E* a chloride of calcium tube, filled with broken glass, which acts as a tower. *g* is a small funnel, attached by rubber and clip to the branch T-tube *h*. Between the T-tube *i* and the wash-bottle for the carbonic acid is placed a short piece of glass tubing, *s*, containing a strip of filter paper, slightly moistened with iodide of starch solution. This tube *s* is really hardly necessary, as no chlorine escapes backwards if a moderate current of carbonic acid is kept passing, but it serves as a check. A glance at the joints *o*, *p*, and *q*, which are of narrow indiarubber tubing, is sufficient to show that, by using this arrangement, practically no rubber is exposed to the action of the chlorine.* *k* is the outlet tube.

The actual operation is performed in the following manner:—The evolution flask is washed and thoroughly dried, and the nitrate (say, about 0·25 gram of nitrate of potassium) is tapped into it from the weighing tube. 1 to 2 c.c. of water are now added, and the bulb is gently warmed, so as to bring the nitrate into solution, after which the stopper of the flask is firmly inserted into it. About 15 c.c., or so, of a solution of potassic iodide (1 in 4) are run into the first condensing tube, any iodide adhering to the upper portion of the tube being washed down with a little water, and 5 c.c. of the same solution, mixed with 8 to 10 c.c. of water, are sucked into the Geissler bulbs, whilst the glass in tower *E* is also thoroughly moistened with the iodide. The Geissler bulbs should be so arranged that gas only bubbles through the last of them. the liquid in the others remaining quiescent.

All the joints having been made tight (there is no difficulty whatever in getting them so), the carbonic anhydride is turned on briskly, and passed through the apparatus until a small tubeful collected at *l*, over caustic potash solution, shows that no appreciable amount of air is left in it. The small outlet tube *l* is now replaced by a chloride of calcium tube, filled with broken glass which has been moistened with the above iodide solution, and closed by a cork through which an outlet tube passes, the object of this "trap" tube being to prevent any air getting back into the apparatus; and the brisk current of carbonic anhydride is continued for a minute or two longer, so as to practically expel all the air from this last tube. The stream of gas is now stopped for an instant, and about 15 c.c. of pure concentrated hydrochloric acid, free from chlorine, run into *A* through the funnel *g* (into the tube of which it is well to have run a few drops of water before beginning to expel the air from the apparatus), and *A* is shaken so as to mix its contents thoroughly. A slow current of carbonic anhydride is now again turned on (1 to 2 bubbles through the wash-bottle per second), and *A* is gently warmed over a burner. It is a distinct advantage that the reaction does not begin until the mixed solutions are warmed, when the liquid becomes orange-coloured, the colour again disappearing after the nitrosyl chloride and chlorine have been expelled. The warming should be very gentle at first, in order to make sure of the conversion of all the nitric acid, and also because the first escaping vapours are relatively very rich in chlorine; afterwards the liquid in *A* is briskly boiled.

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* In some subsequent estimations, the tiny piece of rubber tubing at the joint *o* was done away with, the narrower tube there being accurately ground into the wider one; this makes the condensing apparatus practically perfect.

A very little practice enables the operator to judge as to the proper rate of warming. When the volume of liquid in *A* has been reduced to about 7 c.c., or so (by which time it is again colourless), the stream of carbonic anhydride is slightly quickened, and the apparatus allowed to cool down a little. The burner is now set aside for a few minutes, and 2 c.c., or so, more of hydrochloric acid, previously warmed in a test tube, run in gently through *g*; there is no fear either of the iodide solution running back, or of any bubbles of air escaping through *y*, if this is done carefully. This is a precautionary measure, in case a trace of the liberated chlorine might have lodged in the comparatively cool liquid in tube *h*. The carbonic anhydride is once more turned on slowly, and the liquid in *A* is boiled again until it is reduced to about 5 c.c. It is now only necessary to allow the apparatus to cool down, passing carbonic anhydride all the time, after which the contents of the condensers are transferred to a flask and titrated with thiosulphate. At the end of a properly conducted experiment, the glass in the upper part of tower *E* should be quite colourless, and there should only be a mere trace of iodine showing in the lower part of the tower, while the liquid in the last bulb of the Geissler apparatus ought to be only pale yellow. During the operation, the stopper of *A* and the various joints can be tested for tightness from time to time by means of a piece of iodide of starch paper, and, before disjointing, it is well to test the escaping gas (say, at *m*) in the same way, to make sure that all nitric oxide has been thoroughly expelled.

In order to test the value of the process, pure nitrate of potassium was used, that is, ordinary nitrate recrystallised in small crystals twice, drained, dried in the air-bath, powdered to a fine flour, and again dried at about 160°.

The following examples may be given:—

A. 0·2627 gram nitrate was taken. The liberated iodine required 38·56 c.c. of thiosulphate solution (of which 1 c.c. = 0·006805 gram KNO_3) for conversion. This gave 0·2624 gram nitrate found, or 99·89 per cent.

B. 0·2990 gram nitrate taken.
0·2922 „ „ found, or 100·08 per cent.

C. An analysis of a commercial nitrate of soda gave the following results:—

Moisture at 160°*	2·95	per cent.
Sodic nitrate ($NaNO_3$)	94·68	,,
Sodic chloride ($NaCl$)..........	1·55	,,
Sodic sulphate (Na_2SO_4)........	0·44	,,
Insoluble matter (ignited)	0·44	,,
	99·77	

When it first occurred to me to try this process, I assumed (wrongly) that the decomposition of the nitrate by the hydrochloric acid would be incomplete unless some intermediary, such as a manganous salt, was present. A number of estimations were therefore made in this way, the nitrate in the evolution flask being dissolved in about 5 c.c. of a solution of manganous sulphate (1 part of the crystallised salt in 2), the air expelled from the apparatus, and 15 c.c. hydrochloric acid added as before. Here again, as is already well known, there is no reaction until the solution is warmed, when it becomes of a deep brown-black colour, returning to its original pale-pink at the end of the operation.

The following examples may be cited:—

A. 0·2156 gram nitrate of potassium taken.
0·2154 ,, ,, ,, found, or 99·89 per cent.
B. 0·2760 gram nitrate taken.
0·2750 ,, ,, found, or 99·64 per cent.
C. 0·2514 gram nitrate taken.
0·2508 ,, ,, found, or 99·77 per cent.

The sp. gr. of the hydrochloric acid employed was 1·180 at 11°, which corresponds to about 36 per cent. of HCl; and both the acid and sulphate of manganese solution were absolutely free from chlorine (a blank experiment was made with them alone).

In an estimation of nitric acid by the above method, using nitrate, water, and hydrochloric acid, not more than 1 to 2 c.c. of water should be added, for the solution of the nitrate, to about 15 c.c. of HCl, although 5 c.c. of water may be added with safety. Thus, in an estimation made with 0·2546 gram of potassic nitrate, together with 5 c.c. water and 15 c.c. HCl (that is, a mixed solution containing 27 per cent. HCl), 0·2549 gram was found, or 100·12 per cent. But in another with 8 c.c. water and 12 c.c. hydrochloric acid (that is, a solution containing 19 to 20 per cent. HCl), the reaction was very much slower, and only 90 per cent. of the nitrate was converted.

Similarly, when using a manganous salt as intermediary, it is not advisable to add more than 5 c.c. of the manganese solution for 15 c.c. of hydrochloric acid, as, if more water is present, the reaction goes on very slowly, and, after the dilution has reached a certain point (which I have not exactly determined), the nitric acid is not entirely converted. Thus, in an experiment made with 0·2590 gram potassic nitrate, dissolved in 5 c.c. manganese solution + 12 c.c. acid (that is, in a mixture containing between 19 and 20 per cent. HCl), the reaction was extremely slow. There was relatively little darkening of the solution on warming, but it remained coloured all through the estimation, and was, in fact, distinctly brown at the end of it (that is, after boiling with the second quantity of acid); and in this case only 72·3 per cent. of the nitrate was converted.

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* The moisture in commercial nitrate of soda appears not to be completely driven off at the temperature of an ordinary air-bath (about 95°).

The above process is, of course, only applicable in the absence of organic matter and reducing agents generally. There are two very slight errors involved in it, but these may be neglected, and, indeed, they neutralise one another. In the first place, it seems impossible to get the last traces of air expelled by carbonic anhydride from a Kipp apparatus;* this tends to increase the percentage of nitric acid found. On the other hand, a trace of iodine is always volatilised in transferring the iodide liquid to a flask for titration, a faint iodine odour being always perceptible. And here the advantage of using a rather strong solution of potassic iodide may be again emphasised. The nitric oxide is apparently completely driven out of the apparatus by the carbonic anhydride; at the end of a properly-conducted operation, iodide of starch paper, exposed in the air to the escaping gas, shows no trace of it. The presence of any nitric oxide in the liquid to be titrated is also readily seen by the fact of the blue iodide of starch colour returning *immediately*, after the solution has been decolorised by thiosulphate.

A nitric acid estimation by this method can thus be made either with or without an intermediary like manganous sulphate, but it is better *without* the latter, the nitrate solution being, of course, concentrated. In the presence of a manganous salt, it seems to be more difficult to boil out the last traces of chlorine.

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* Messrs. De Koninck and Nihoul call attention in their paper to a point which I had overlooked, namely, to the necessity for making the connections between the Kipp apparatus and the wash-bottle, and between the latter and the evolution flask *A*, with as short pieces of rubber tubing as possible, so as to avoid the diffusion of air into the apparatus. The pieces of tubing used by myself in the above experiments were too long. By attending to this; by exhausting the marble to be used for the generation of the carbonic anhydride in a vacuum, as recommended by Bernthsen; and by boiling out the hydrochloric acid for the "Kipp" (and also the water for the wash-bottle), and cooling it again in the absence of air, the analytical error arising from the presence of traces of air might be practically done away with. Further, to prevent any re-absorption of air by the acid in the topmost bulb of the Kipp apparatus, a second smaller carbonic acid "Kipp" may be attached to the latter, the connecting stop-cock between the two "Kipps" being left always open.

It is hardly necessary to add that the greatest care must be taken in standardising the thiosulphate solution from a decinormal dichromate one. I have found a fifth-normal solution of the thiosulphate to be most convenient (this contains 50 grams of the salt per litre). 0·25 gram of potassic nitrate requires about 38 c.c. of such a solution.

It appears to me that there are several advantages in this method of estimating nitric acid in nitrates, of course always in absence of reducing agents:—1st. The time required is short; once the apparatus has been made, an estimation can be done in 1½ to 2 hours. 2nd. Bunsen's titration of iodine is the most beautiful of all volumetric methods. 3rd. The process is comparatively simple, and can be readily carried out by any one fairly expert in chemical analysis. I trust that it may be found of practical use for the direct estimation of nitric acid in commercial nitrates of potash and soda.

University College of N. Wales, Bangor,
April 28, 1891.

XLIX.—*The Decomposition of Silver Chloride by Light.*

By A. Richardson, Ph.D., University College, Bristol.

Although the fact that silver chloride darkens on exposure to light has long been known, the composition of the product formed has not yet been satisfactorily determined; the observation of Schelle, however, that the darkening process is accompanied by an evolution of chlorine, leads to the conclusion that the substance formed is either a subchloride or an oxychloride of silver, whilst its sparing solubility in dilute nitric acid seems to preclude the possibility of the reduction of the chloride to metallic silver.

Fischer, in 1814, assumed that the darkened product was a subchloride, and this idea has been generally accepted until recent years. When, however, doubt was cast on the existence of Wöhler's silver suboxide by the experiments of Muthman (*Ber.*, 1887, **20**, 983), and of Bailey and Fowler (Trans., 1887, **51**, 416), and the existence of the suboxide of Pfordten (*Ber.*, 1887, **20**, 1458, 3375; 1888, **21**, 2288) was disproved by Freidheim (*Ber.*, 1887, **20**, 2554), the evidence in favour of the subchloride theory was somewhat shaken.

Quite recently, however, Güntz (*Compt. rend.*, **112**, 861) claims to have obtained silver subchloride by the action of gaseous hydrogen chloride on silver subfluoride, as also the suboxide and other similar compounds; the subchloride so obtained has not, however, been identified with the darkened product formed by the action of light on silver chloride.

The other view, namely, that the compound formed is an oxychloride of silver, has lately been received with considerable favour, and seems to be supported by some experiments of Dr. Hodgkinson, in which the presence of the oxychloride appears to have been detected in the darkened compound (Meldola, *Chemistry of Photography*, p. 856). As, however, the evidence in favour either of the subchloride or oxychloride theory is far from conclusive, it was thought desirable to examine the darkened silver chloride, in order to determine whether it contained oxygen, and further, to study the decomposition of the chloride when exposed to light under water.

The silver chloride used in all the experiments was obtained by adding hydrochloric acid to a solution of pure silver nitrate, the precipitate being washed by decantation, till free from acid.

Action of Silver Chloride on Water when Exposed to Light.

In the early experiments, the chloride was exposed to light in sealed tubes containing water, the space above being occupied by air. When opened after long exposure (about six months), it was found that a considerable quantity of gas had been formed, and that it contained sufficient oxygen to rekindle a glowing match (8 grams of the chloride gave 7 c.c. of gas). The evolution of oxygen under these conditions was confirmed by later experiments, and was studied more closely in conjunction with the other changes which occur.

An experiment is recorded by Robert Hunt (*Researches on Light*, p. 81), in which absorption of gas was observed to take place when the chloride was darkened, leading him to the conclusion that the product contained oxygen; the conditions, however, were somewhat different, and this may account for the want of agreement between our results.*

During the exposure of the chloride under water, it had been frequently observed that the volume of liquid present exercised a considerable influence on the rate at which the substance darkened; this point was, therefore, further investigated. The exposure of the chloride was made in tubes closed at one end, and so arranged that any gas which might be evolved would expel a portion of the water by an exit tube terminating in a bulb, in which it was collected. Four tubes of this form, having a capacity varying from 57 c.c. to 350 c.c., were filled completely with water containing equal quantities (5 grams) of silver chloride in suspension. After half an hour's exposure to bright sunlight, bubbles of gas collected in the tube, and continued to be evolved till the end of the experiment. The gas was measured after eight days' exposure (April 10—17), and the liquid was examined for free* chlorine by the addition of potassium iodide and titration with N/10 sodium thiosulphate in the usual way. The total chlorine was also estimated, the combined chlorine being found by difference. In determining the total chlorine, the method adopted in all cases was to add sulphur dioxide to a known volume of the liquid, the excess being removed by potassium chromate; sodium hydrate was next added, and the solution boiled; the precipitated chromic hydrate was filtered off, and the liquid and washings made up to known volume; the chlorine was then estimated with N/10 silver nitrate solution, the liquid having been previously acidified with dilute nitric acid, and neutralised with sodium carbonate.

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* It does not appear that in Hunt's experiment a large volume of water was present.

This method was found to give good results provided the reagents used were free from chlorine. The results are given in the following table:—

TABLE I.

1. H_2O.	2. O at 0° and 760 mm.	3. Total Cl.	4. Combined Cl.	5. Free Cl.	6. HCl in 100 parts of solution.
c.c.	c.c.	gram	gram	gram	gram
57	4·02	0·097	0·092	0·005	0·162
121	5·74	0·124	0·122	0·0017	0·101
152	5·94	0·127	0·126	0·0010	0·083
356	6·61	0·142	0·142	0·0000	0·039

It will be seen that the effect of an increasing volume of water is to increase the total quantity of chlorine in solution, and therefore the amount of silver chloride decomposed, also to increase the total amount of hydrochloric acid formed and of oxygen liberated;† there is, however, a diminution in the amount of free chlorine present. Further it is seen, on calculating the strength of acid per 100 parts of water (Column 6), that the strongest acid is found in the tube containing the smallest quantity of water, and it is here also that the largest quantity of free chlorine is present. The strength of acid and the amount of free chlorine therefore decrease as the volume of water increases.

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* The "free" chlorine is not necessarily present entirely as such, but may exist partly in the form of oxygen acids of chlorine.

† This only represents a portion of the oxygen formed, as the amount of gas dissolved in the water was not determined.

As the decomposition of silver chloride by light is to a large extent dependent on the proportion of free chlorine present, the conditions which regulate its conversion into hydrochloric acid in the solution were studied.

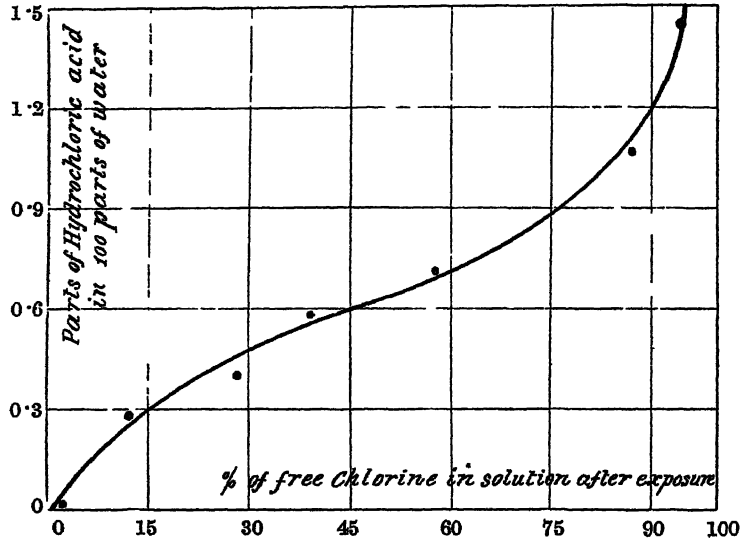
It is known that the presence of hydrochloric acid exercises a retarding influence on the decomposition of chlorine-water by light, and a series of experiments have been made (*B. A. Report*, 1888), in order to determine the influence of different quantities of acid on its stability. The results given in Table II show that even minute quantities of the acid exercise a very decided influence on the rate at which free chlorine is converted into hydrochloric acid under the influence of sunlight (exposure seven days, August 17—24).

TABLE II.

Parts of Cl per 100 H_2O.	Parts of HCl per 100 H_2O added.	Per cent. free Cl found.	Per cent. combined Cl found − HCl added.
0·284	0·029	2·34	97·66
0·270	0·289	12·61	87·35
0·260	0·400	28·57	71·42
0·290	0·587	39·25	60·95
0·290	0·724	58·71	41·29
0·282	1·158	87·82	12·18
0·291	1·447	95·47	4·53

In the case of silver chloride in water, the chlorine evolved during exposure to light is at first speedily converted into hydrochloric acid, but as the strength of acid increases its rate of formation diminishes. Free chlorine, therefore, accumulates in the solution until (the intensity of light remaining constant) a maximum is reached, at which stage further decomposition of silver chloride is balanced by recombination of chlorine with the darkened product. The formation of free chlorine is still more marked where silver chloride is exposed under a solution of hydrochloric acid in the first instance, as is shown by the following experiment, in which equal quantities of silver chloride were exposed to light in solutions of hydrochloric acid of varying strengths. After an exposure of seven days (April 20—27) the free chlorine and oxygen liberated were determined. During exposure it was observed that the liquid in the tubes containing acid was of a distinctly green tint (especially when seen through the

Curve showing influence of Hydrochloric Acid on the decomposition of Chlorine-water by Light.



entire length of the tube), the chlorine liberated from the silver salt remaining in solution in the water. In the night, however, rechlorination of the darkened silver compound had occurred to such an extent that the colour had almost entirely disappeared from the solution. The estimation of the free chlorine was therefore made immediately after exposure to bright sunshine, and again after the liquid had been left in contact with the darkened product for 14 hours in the dark.

The results obtained are given in the following table:—

TABLE III.

1. HCl added per 100 c.c. solution.	2. c.c. O set free.	3. Free Cl found.	4. Free Cl found after 14 hours in the dark.
4·0	minute bubble	0·042	0·014
1·97	0·5	0·035	0·019
0·38	1·9	0·024	0·003
0·19	1·7	0·007	0·0008
0·00	4·2	0·0017	0·0003

In another experiment made to determine how far the total amount of chlorine evolved from silver chloride during exposure was influenced by the presence of hydrochloric acid, the following results were obtained. A comparative experiment was made with silver chloride in pure water.

TABLE IV.

HCl per 100 pts. H_2O taken.	Total Cl found (–HCl added).	Combined Cl found.	Free Cl found.	Per cent. free Cl.
0·909 gram	0·201 gram	0·173	0·027	13·7
0·0 „	0·276 „	0·273	0·002	0·94

Here it is seen that, although the presence of hydrochloric acid increases the amount of free chlorine in the solution, yet the total chlorine set free (and therefore the amount of decomposition of the silver salt), is decreased. In order then to obtain the maximum amount of surface decomposition of silver chloride, it is necessary that the volume of water present should be relatively large, and that the solution of acid formed should be often replaced by pure water during the exposure.

The explanation of the retarding influence of haloïd salts, and of oxidising agents, on the darkening of silver chloride appears to be found in a study of the action of these substances on solutions of chlorine-water under the influence of light.

The condition of the free chlorine in the solution is one of some interest, and was next studied. The examination of the liquid for oxy-acids of chlorine was, however, hampered by the fact that a part of the oxygen liberated was present as ozone, the smell of this substance being distinctly recognised, especially during the first periods of exposure of silver chloride, when large quantities of water were present. To further prove the presence of this substance, air was drawn through water containing silver chloride in suspension, during exposure to sunlight, and was then passed through two bulbs containing solutions of silver nitrate, and finally into a solution of potassium iodide, which was protected from the light; the liquid in the first bulb became milky, that in the second remained perfectly clear, whilst iodine was set free in the solution of potassium iodide.

No hydrogen peroxide was detected in the liquid containing silver chloride during any period of exposure.

The observations of Popper (*Annalen*, **227**, 161) and of Pedler (Trans., 1890, **57**, 613) show that hypochlorous and other oxy-acids of chlorine are formed during the decomposition of solutions of chlorine-water by light, and it seemed probable that a part of the chlorine evolved by the decomposition of silver chloride by light should, in presence of water, form similar products, and statements to this effect have repeatedly been made (*B. A. Report*, 1859, 107). An experiment was therefore made in which silver chloride in contact with a small quantity of water (20 c.c.) was exposed to bright sunlight for six hours. The liquid was then tested for hypochlorous acid by agitation with mercury, and subsequent treatment with hydrochloric acid, as suggested by Wolters (*J. pr. Chem.*, 74, 68). The formation of hypochlorous acid was noted by the fact that mercury was present in the solution; although this test could not be applied quantitatively in the presence of ozone, yet the comparatively large quantity of mercury in the solution could only be ascribed to the presence of hypochlorous or similar acids in the liquid, together with free chlorine. It was noticed, however, that a strong solution of hypochlorous acid was decomposed by contact with normal silver chloride, even in the dark, a green gas containing free oxygen and chlorine being evolved; the silver chloride appeared to be unaltered; how far dilute solutions of the acid are decomposed is yet to be determined.

Examination of the Darkened Chloride for Oxygen.

The question whether the darkened compound is an oxychloride, or a subchloride of silver appeared to be best decided by a careful examination of the compound for oxygen. The first experiments made in this direction consisted in heating the dry, darkened product in a vacuum, and collecting any gas which might be given off.

26 grams of pure silver chloride, which had been exposed to light under water until it had lost 8 per cent. of its total chlorine, was dried at 110°, and placed in a hard glass tube closed at one end, and connected at the other with a Sprengel pump; after the tube was exhausted, a graduated tube containing mercury was inverted over the (turned up) end of the fall tube of the pump, in order to collect any gas which might be given off on heating. On gently warming the tube containing the chloride, it was found that just at first small quantities of gas were carried over; when gas ceased to come off, the temperature was raised and kept at the melting point of the chloride for about half an hour, during which period no further gas was evolved. The total volume of gas collected = 0·6 c.c.; this was proved to be air contained in the powder and on the glass, for on shaking with alkaline pyrogallol only a minute contraction of about 0·1 c.c. took place.

In a second experiment, 20 grams of the darkened chloride, from which 7 per cent. of total chlorine had been removed by exposure to light, was heated as in the previous experiment; in this case also a minute quantity of gas was given off, which measured 0·4 c.c. at 0° and 760 mm.

It appears from these results that if oxygen is present in combination with the darkened chloride, it is not given off at the melting point of the silver chloride with which it is associated.

The next experiments were made to determine whether water was formed when the darkened product was heated in pure hydrogen. The gas, which was prepared by the action of steam on metallic sodium, was first dried by passing it through tubes containing sulphuric acid, then lead over metallic copper heated to redness, and, finally, the last traces of moisture were removed by means of phosphorus pentoxide. The gas so obtained was passed into a combustion tube, in which the darkened chloride was to be heated; this tube was drawn out at one end and terminated inside a bulb, which was connected with a weighed phosphorus pentoxide tube, the escaping gas then passing through a second drying tube and finally into a bulb containing water, in which the hydrochloric acid was absorbed.

That phosphorus pentoxide does not absorb dry hydrogen chloride to any appreciable extent (when exposed to the gas for a few hours only) was proved by the fact that the gain in weight of such a drying tube, after being exposed to the action of hydrogen chloride for 3½ hours, was only 0·003 gram, and that, on again passing the gas for 2 hours, no further increase in weight could be detected.* Tubes which had been exposed to the action of the gas till the weight remained constant were used in the subsequent experiments. Before heating the darkened silver chloride in hydrogen, the combustion tube was exhausted and gently heated until the air adhering to the glass and pulverised chloride had been removed; the tube was then heated in the current of hydrogen, the temperature being gradually raised till the chloride began to show signs of fusing; it was important, however, that the temperature should not rise too high, as the hydrogen chloride formed was found to act on the glass, carrying over small quantities of calcium chloride, which possibly (in one case) reached the weighed phosphorus pentoxide tube. The reduction, which lasted from 7—8 hours, was found to be complete when the escaping gas failed to give any turbidity with silver nitrate.

The results are given of four experiments made in the manner described. In the first three, the darkened chloride was obtained from silver chloride, from which 8 per cent. of chlorine had been removed by the action of light. In the last experiment, pure silver chloride was reduced in order to determine how far the gain in weight in the phosphorus pentoxide tube was due to experimental error.

In the second experiment, the tube had been strongly heated, and it was most probable that a trace of calcium chloride was carried over.

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* Dry air was drawn through the tubes before weighing.

TABLE V.

Weight of darkened chloride taken.	Gain in weight of P_2O_5 tube.
1. 24·64 grams	0·00375 gram
2. 22·35 „	0·00475 „ (very strongly heated)
3. 24·24 „	0·00325 gram
4. 13·0 „ (normal chloride)	0·00250 „

From these experiments, it will be seen that the increase in weight in the phosphorus pentoxide tubes is so small as to preclude the possibility of the presence of an oxygen compound of silver in the darkened chloride.

In conclusion, it may be mentioned that, as a further proof of the absence of oxygen in this substance, an experiment, which is a modification of one described by Cary Lea (*Amer. J. Sci.* **38**, 356—361), was made. Silver chloride was dried with extreme care and placed in a tube containing pure dry carbon tetrachloride, from which all air was expelled by boiling; on exposure to light, the chloride rapidly darkened, although it was certain that no oxygen was present.

L.—*Interaction of Phenylthiocarbimide with Acetic and Propionic Acids respectively.*

By EMIL A. WERNER, Assistant Lecturer in Chemistry, University of Dublin.

THE interaction of phenylthiocarbimide with acetic acid was originally made the subject of an experiment by A. W. von Hofmann (*Ber.*, 3, 770) and later on by Claus and Völtzkow (*Ber*, **14**, 445). According to the former, the substances interact at 130—140° with production of *diacetanilide*, in accordance with the equation

$$C_6H\cdot NCS + 2CH_3\cdot COOH = (CH_3\cdot CO)_2N\cdot C_6H_5 + H_2S + CO_2.$$

Claus and Völtzkow* heated the mixture at 160°, and showed that under these conditions the product is *acetanilide*, while CO_2, H_2S, and COS are the bye-products of the decomposition.

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* These chemists appear to have overlooked Hofmann's experiment, as their paper contains no reference to it.

In neither case were the experiments exhaustive, analytical data being absent from both papers.

In order to finally establish the exact nature of the action, I have, in connection with the previous paper (this vol., p. 396), made a careful reinvestigation of the subject; in the meantime, I have been, to a certain extent, anticipated in my work by the recent publication of a paper by Messrs. Cain and Cohen dealing with the same change (this vol., p. 327).

While I agree with these gentlemen that diacetanilide is not formed under any conditions of interaction between phenylthiocarbimide and glacial acetic acid, my results, on the other hand, compel me to differ entirely from their conclusions with respect to the exact course of the change.

Since the thiocarbimides are readily decomposed by water at moderately high temperatures, a careful exclusion of water in studying these actions is of paramount importance; the neglect of this precaution has, I believe, caused Messrs. Cain and Cohen to be misled by their results.

The details of my experiments are as follows:—

I. *Phenylthiocarbimide and Anhydrous Acetic Acid.*

In all the experiments recorded in my previous paper (this vol., p. 396), the conditions were such that water was obviously absent from the materials. In preparing, therefore, a specimen of pure acetic acid for the present work, the following method was adopted. The fraction distilling at 118—121° from a specimen of commercial pure acetic acid was subjected to a second distillation, and a fraction collected which distilled over at 119°.

A careful titration of the acid in this fraction showed it to contain 98·4 per cent. of real acetic acid. The necessary amount of pure acetic anhydride to yield a 100 per cent. acid was now added to a weighed quantity of this fraction, and the product heated on the water-bath in a sealed tube for several hours.

The results of my experiments prove conclusively that my specimen of acid was absolutely anhydrous.

Exp. 1.—Since I have already stated in the previous paper that the action takes place according to the equation

$$C_6H_5{\cdot}NCS + CH_3{\cdot}COOH = CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + COS,$$

equal molecular proportions were accordingly used in the first experiments.

The quantities employed were:—

$$\begin{cases} 6{\cdot}8 \text{ grams } C_6H_5{\cdot}NCS \ldots & 1 \text{ mol. prop.} \\ 3{\cdot}0 \quad ,, \quad CH_3{\cdot}COOH \ldots & 1 \quad ,, \end{cases}$$

Phenylthiocarbimide and pure acetic acid are freely miscible in these proportions. The mixture was heated in a sealed tube of stout glass at 135—140° for three hours. On cooling, the contents had become a solid, crystalline mass of a pale yellow tint. There was a considerable rush of gas on opening the tube. The following observations on this gas prove that it was, practically, pure COS. With a *neutral* solution of lead nitrate, it produced no precipitate, and hence *sulphuretted hydrogen was absent*. With an *alkaline* lead solution and with ammoniacal silver nitrate, it produced an immediate *black* precipitate of sulphide of the metal. The gas burnt with a lavender-blue flame, producing CO_2 and SO_2, but *no water*, as shown by the absence of a deposit of "dew" on the sides of a funnel held over the flame. The odour, while characteristic of COS, was perfectly free from the smell of H_2S.

The weight of the solid product, after gentle warming to expel every trace of occluded gas, was 6·9 grams.

Hence loss due to gas evolved was 9·8 – 6·9 = 2·9 grams, or 29·59 per cent. of the materials used. Theory for the above equation, 30·76 per cent.

The solid product was *completely* dissolved in sufficient boiling distilled water, from which it separated on cooling in thin, glistening prisms melting at 112—113°, and possessing all the properties of acetanilide. From the mother liquor, two further crops of crystals were obtained; the melting point was in each case, after a single recrystallisation, 112—113°.

The following analytical data prove conclusively that acetanilide is the sole constituent of the solid product of the interaction:—

1st crop of crystals:—0·2098 gram gave 19·1 c.c. nitrogen at 18° and 766 mm.

2nd crop of crystals:—0·1928 gram gave 17·9 c.c. nitrogen at 15° and 757 mm.

3rd crop of crystals:—0·1725 gram gave 16·0 c.c. nitrogen at 14° and 751 mm.

		Theory for acetanilide.	Theory for diacetanilide.
1st. N....	10·53 per cent.	10·37 p. c.	7·90 p. c.
2nd. N....	10·75 „		
3rd. N....	10·72 „		

These determinations of nitrogen were necessary for identification, since v. Hofmann states that diacetanilide melts at 111—112°, and resembles acetanilide in its properties.

The total weight of acetanilide crystals obtained was 6·78 grams, corresponding to 69·18 per cent. of the materials used.

Theory for the above equation, 69 23 per cent.

Exp. 2.—This was a repetition of the preceding experiment, as regards the molecular proportions and quantities used; the mixture, however, was heated for two hours at 160—170°, the same temperature as that adopted by Claus and Völtzkow in their experiment. The results are practically the same as at the lower temperature, namely:—

Gas evolved........	2·95 grams.	Theory....	3·0 grams.
Acetanilide crystals.	6·69 „	„	6·75 „

Exp. 3.—In this case, *two* molecular proportions of acetic acid were used to one of the thiocarbimide, these being the ratios demanded by the equation given by v. Hofmann.

$$\text{The quantities used were} \begin{cases} 3{\cdot}4 \text{ grams } C_6H_5{\cdot}NCS \\ 3\,0 \quad „ \quad CH_3{\cdot}COOH. \end{cases}$$

Heated for three hours at 135—140°.

The product of the action was a viscid liquid, until the gas had been expelled from the tube, when it almost completely solidified. It smelt strongly of acetic acid, and, in order to estimate the amount of the latter, the product was extracted with cold water, and the solution filtered from excess of acetanilide was directly titrated with standard soda; 1·41 grams of unaltered acetic acid was present, or practically half the quantity used.

The weight of acetanilide obtained was 3·2 grams. Theory, 3 37 grams. Therefore the interaction was simply between equal molecular proportions.

Exp. 4.—The reverse of the last; namely, two molecular proportions of phenylthiocarbimide to one of acetic acid.

$$\text{Quantities used} \begin{cases} 6{\cdot}8 \text{ grams } C_6H_5{\cdot}NCS \\ 1{\cdot}5 \quad „ \quad CH_3{\cdot}COOH. \end{cases}$$

Heated for three hours at 135—140°.

The product of the action was a soft solid, about the consistency of suet. It smelt strongly of phenylthiocarbimide, and was therefore added to water and subjected to steam-distillation.

2·98 grams of $C_6H_5{\cdot}NCS$ were collected from the distillate; the almost unavoidable error in collecting a small quantity of the thiocarbimide is sufficient to account for the slight deficiency (0·42 gram) from the theoretical, for one molecular proportion.

Weight of acetanilide obtained, 3·17 grams. Theory, 3·37 grams. Therefore interaction was again restricted to equal molecular proportions.

Since the previous investigators* agree in mentioning sulphuretted hydrogen as one of the gaseous products of decomposition, the absence of which I proved in all the foregoing experiments, it seemed probable that the occurrence of this gas must be attributed to the presence of water in the materials. With the object of studying this point, and of further testing the possibility of the formation of diacetanilide under such conditions, the following experiments were conducted:—

II. *Phenylthiocarbimide and Acetic Acid containing* 10 *per cent. of Water.*

Exp. 5.—Quantities used
- 3·4 grams $C_6H_5{\cdot}NCS$ (1 mol. prop.).
- 1·5 „ $CH_3{\cdot}COOH$ (1 mol. prop.).
- 0·15 „ H_2O.

The thiocarbimide is not completely miscible with acetic acid diluted to the above extent. The mixture was heated in a sealed tube at 135—140° for three hours. On opening the tube, there was abundant evolution of gas, *containing much sulphuretted hydrogen*, recognised by following tests:—

a. The characteristic smell.

b. With *neutral* lead nitrate solution, an immediate black precipitate of PbS.

c. On combustion of the gas, *water was formed*, together with SO_2 and CO_2.

The gas evolved from the tube consisted of H_2S, CO_2, and COS.

The strong odour of acetic acid in the solid product of the action proved that a certain portion had escaped decomposition, which was not the case when the same molecular proportions were caused to act in the absence of water.

The solid product, after complete extraction with boiling water, left 0·68 gram of an insoluble substance which evidently resulted from secondary action due to the presence of water. The total weight of acetanilide obtained from the aqueous extract was 2·27 grams.

That this consisted solely of acetanilide was proved by a nitrogen determination in a mean sample taken from the whole product.

	Found.	Theory.
N	10·63 per cent.	10·37 per cent.

The main portion of the work in the present paper was completed in the autumn of last year.

Therefore, no diacetanilide (N = 7·9 per cent.) was present in the product.

A quantity of the insoluble product, accumulated from three experiments, was purified by crystallisation from hot alcohol, from which it separated almost completely, on cooling, in the form of fine, slender, colourless prisms having a beautiful, silky lustre. The crystals do not contain sulphur.

The analyses of a specimen, purified by two crystallisations from boiling alcohol, lead to the empirical formula $C_{13}H_{12}N_2O$ for the substance.

Data:—

I. 0·2429 gram gave 0·124 gram H_2O (the carbon of this experiment was lost).

II. 0·2035 gram gave 0·1108 gram H_2O and 0·546 gram CO_2.

III. 0·1865 gram gave 21·6 c.c. of nitrogen at 16° and 755 mm.

	Found. I.	Found. II.	Found. III.	Theory for $C_{13}H_{12}N_2O$.
C......	—	73·16	—	73·58 per cent.
H......	5·66	6 04	—	5·66 ,,
N......	—	—	13·35	13·20 ,,
O......	—	7·45 (by diff.)		7·55 ,,

The crystals melt at 234—235°, and, when fused with phosphoric anhydride, evolve at once the irritating odour of phenyl isocyanate.

These results, verified by a direct comparison with a specimen of carbanilide melting at 235°, prove the identity of the substance.

The formation of diphenylurea, shown by this experiment to be due to the presence of water, is readily explained by the equation

$$2C_6H_5{\cdot}NCS + 3H_2O = CO(NH{\cdot}C_6H_5)_2 + 2H_2S + CO_2,$$

the correct nature of which is proved by the quantitative results obtained. Thus, according to this equation, 0·15 gram water should give rise to the formation of

Diphenylurea.. 0·588 gram. Found.. 0·68 gram (crude).

whilst, under the circumstances, the weight of acetanilide produced should be—

Theory........ 2·52 grams. Found.. 2·27 grams.

A closer agreement with the theoretical numbers was not to be expected in an experiment of this nature, where great accuracy was not aimed at.

I may add that three other experiments were carried out in presence of water, and in each case H_2S and diphenylurea were produced, the quantity of the latter varying directly with the amount of water present; it is unnecessary to give the details of these experiments, as the next point of interest in connection with the present investigation lies in the following:—

Exp. 6.—Quantities used $\left\{\begin{array}{lll} 3\cdot4 & \text{grams} & C_6H_5{\cdot}NCS. \\ 1\cdot5 & ,, & CH_3{\cdot}COOH. \\ 0\cdot15 & ,, & H_2O. \end{array}\right.$

Heated in sealed tube for three hours at 160—170°, that is, at the temperature as adopted by Claus and Völtzkow. Under these conditions, the weight of carbanilide obtained was only

0 09 gram. Theory .. 0·588 gram,

whilst the weight of acetanilide was increased to 2 95 grams. As before, the gas evolved consisted of CO_2, H_2S, and COS.

Therefore, at the *higher* temperature, the diphenylurea undergoes decomposition, giving rise to acetanilide, in accordance with the equation

$$CO{<}^{NH\cdot C_6H_5}_{NH\cdot C_6H_5} + 2CH_3{\cdot}COOH = 2CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + CO_2 + H_2O.$$

This decomposition is independent of the presence of water, as a direct experiment has shown that pure anhydrous acetic acid decomposes diphenylurea at 160—170°, though for complete decomposition a large excess of the acid and prolonged heating is required.

III. *Phenylthiocarbimide and Propionic Acid.*

Quantities used $\left\{\begin{array}{lll} 6\cdot8 & \text{grams} & C_6H_5{\cdot}NCS. \\ 3\cdot7 & ,, & C_2H_5{\cdot}COOH. \end{array}\right.$

The specimen of propionic acid was obtained from Messrs. Harrington Bros., of Cork; a determination of its strength proved it to contain 99·56 per cent. of real acid. The mixture was heated at 130—140° for two hours. A *trace* of sulphuretted hydrogen was evolved, due to the small quantity of water present. The weight of diphenylurea obtained was 0 11 gram. The weight of propionanilide (m. p. 99—100°)

6·85 grams. Theory...... 7·45 grams.

The product from the action smelt slightly of phenylthiocarbimide, and contained a small amount of unaltered acid; complete action, therefore, had not taken place.

The results of this single experiment prove that with propionic acid interaction takes place in exactly the same manner as with acetic acid.

In the case of a single experiment with phenylthiocarbimide and a sample of formic acid containing 99·1 per cent. of real acid, there was obtained, besides formanilide and diphenylurea, a small quantity of sulphocarbanilide.

Therefore, in this case a further secondary decomposition appears to take place, not noticed with either acetic or propionic acids.

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LI.—*New Benzylic Derivatives of Thiocarbamide.*

By Augustus E. Dixon, M.D., Professor of Chemistry, Queen's College, Galway.

When describing, some little time ago (Trans., 1889, **55**, 300), the preparation and properties of methylbenzyl- and ethylbenzyl-thiocarbamides, I took occasion to point out that the number of benzylated derivatives of thiocarbamide hitherto recorded is extremely limited.

Bernthsen and Klinger (*Ber.*, **12**, 575) obtained from benzyl chloride and thiocarbamide a compound of the same ultimate composition as monobenzylthiocarbamide. A series of addition-products was next recorded by Reimarus (*Ber.*, **19**, 2348), resulting from the combination of dibenzylthiocarbamide with various alkylogens; and recently E. A. Werner (Trans., 1890, **57**, 295), in the course of an interesting investigation on the compounds of alkylogens with thiocarbamides, obtained compounds having the same empirical formulæ as benzylphenyl- and benzyldiphenyl-thiocarbamide. These substances, however, do not, properly speaking, belong to the class of substituted thiocarbamides, but are sulphine compounds isomeric with the latter; they are strongly basic, easily decomposed, and, so far as comparison is at present possible, their melting points appear to lie much lower than those of the isomeric true thiocarbamides.

The only benzyl substitution derivatives, in fact, of thiocarbamide which have been hitherto described (other than the methyl and ethyl compounds referred to above) are the monobenzyl- and two dibenzylthiocarbamides; and it is remarkable that our information concerning two out of these three requires correction.

Preparation of Benzylthiocarbimide.—The yield of benzylthiocarbimide is very sensitive to the conditions under which it is prepared; after several trials, the following method was found to give the best result:—

Benzylamine and rather more than the calculated quantity of carbon bisulphide, each dissolved in a large bulk of ether and strongly cooled by a freezing mixture, are gradually mixed, with constant stirring. The separated benzylammonium benzyldithiocarbamate is air-dried, introduced into a large flask, dissolved in alcohol, and to the boiling solution is added, little by little, the calculated quantity of mercuric chloride in very fine powder. Black mercuric sulphide separates at first, but when about one-half to two-thirds of the chloride has been used a white precipitate begins to form. When the mercuric chloride has all been added, the mixture is steam-distilled, the white precipitate (which appears to consist of a compound of benzylamine hydrochloride with mercuric chloride) is decomposed, and the greyish mixture gradually changes to a full black. The distillation is rather tedious, even in a rapid steam-current only about 4 grams of thiocarbimide per hour being obtained on the average. The yield by the method described is very satisfactory, amounting to over 70 per cent. of the theoretical.

Benzylammonium benzyldithiocarbamate, though gradually decomposed by boiling with alcohol, may nevertheless be purified by careful recrystallisation from warm alcoholic solution. A quantity so treated came down in beautiful, thin, iridescent plates; these, when dried and powdered, melted at 118—119° with copious effervescence and evolution of hydrogen sulphide. After expulsion of the gas, the liquid again solidified, and the product now melted at about 142—144°.

There could be little doubt that the substance of higher melting point was dibenzylthiocarbamide,

$$CS<\begin{matrix}NH\cdot C_7H_7\\ S\cdot NH_3\cdot C_7H_7\end{matrix} = CS<\begin{matrix}NH\cdot C_7H_7\\ NH\cdot C_7H_7\end{matrix} + H_2S,$$

though this compound is stated by Strakosch (*Ber.*, 5, 696) to melt at 114°. To decide the point, a quantity of dibenzylthiocarbamide, prepared in the usual way from benzylamine and carbon bisulphide, was purified by recrystallisation from alcohol. The product melted at 146—147° (uncorr.).

Benzylthiocarbimide and Ammonia.—Benzylthiocarbamide.

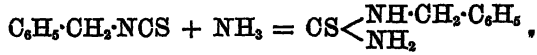
To prepare this substance, benzylthiocarbimide was covered with excess of strong ammonia solution; in about an hour, the thiocarb imide had disappeared, and was replaced by a white, crystalline cake. On recrystallising this from boiling water, minute, white prisms were obtained; the latter were quite pure, and melted at 161—162° (uncorr.).

A portion dried at 100° was burnt for nitrogen, with the following result;—

0·2200 gram, burnt with copper oxide, and copper gauze in front, afforded 32·2 c.c. gas, measured at 13° and 752·5 mm., or N = 17·12 per cent.

Calculated for $C_8H_{10}N_2S$, N = 16·90 per cent.

The product is, accordingly, monobenzylthiocarbamide,



$$C_6H_5{\cdot}CH_2{\cdot}NCS + NH_3 = CS{<}\begin{matrix}NH{\cdot}CH_2{\cdot}C_6H_5\\NH_2\end{matrix},$$

The substance is slightly soluble in boiling water, almost insoluble in cold; it dissolves easily in alcohol, rather sparingly in benzene, chloroform, or carbon bisulphide, and very sparingly in ether.

Neither aqueous nor alcoholic solution gives any colour-change with ferric chloride; on the addition of ammoniacal silver nitrate, the liquid is immediately blackened; and it is gradually desulphurised by boiling with alkaline solution of lead.

The properties of this compound are by no means in agreement with those of the product described by Paternò and Spica as resulting from the combination of benzylamine hydrochloride with potassium thiocyanate. These chemists state (*Ber.*, 9, 81) that the monobenzyl thiocarbamide so obtained is very soluble in water, and record its melting point as 101°. The possibility of 101° being a misprint for 161° suggested itself, but the discrepancy regarding its solubility in water still remained. With a view, therefore, of ascertaining the cause of this, the preparation from benzylamine hydrochloride and potassium thiocyanate was undertaken, with the following somewhat unexpected result:—

Benzylamine Hydrochloride and Potassium Thiocyanate.—Benzylammonium Thiocyanate.

10·7 grams (1 mol.) of pure benzylamine were neutralised by dilute hydrochloric acid, 9·7 grams (1 mol.) of potassium thiocyanate in aqueous solution were added, and the mixture heated on the water-bath until the water was expelled. The product, an oily liquid mixed with solid matter, when removed and cooled, set to a hard, brittle cake. This was powdered, boiled up with successive quantities of anhydrous alcohol, filtered from potassium chloride, and the mixed alcoholic extracts concentrated by gentle heating. When the latter had become reduced to a very small bulk, crystals separated; these were removed, washed well with chloroform, and recrystallised twice from the same solvent mixed with a trace of alcohol. Very long, hair-like, flexible needles were thus obtained, possessing a beautiful silky lustre, and melting at 101—102° (uncorr.) without sensible decomposition.

The product is *benzylammonium thiocyanate*:—

I. 0·2042 gram, burnt with CuO, and copper gauze in front, afforded 29·1 c.c. nitrogen, measured at 13° and 773 mm., or N = 17·12 per cent.

II. 1·0376 grams were dissolved in 250 c.c. of water, 98·85 c.c. of this solution were required to saturate 25 c.c. of N/10 $AgNO_3$, or SCN = 35·31 per cent.

III. 25 c.c. of same solution, titrated by Barnes and Liddle's method, required 25·7 c.c. of $CuSO_4$ solution (1·5365 grams Cu per litre), or SCN = 34·84 per cent.

	Calculated for $C_7H_7{\cdot}NH_2{\cdot}HSCN$.	Experiment.	
		I.	II.
N	16·90	17·12	—
SCN	34·96	35·31	34·84

The substance is very freely soluble both in hot and cold water, and in alcohol; it is somewhat sparingly soluble in boiling chloroform, still less so in cold, it floats on this solvent; the addition of a trace of alcohol greatly increases the solubility. In ether, benzene, and carbon bisulphide, it dissolves very sparingly.

Its solution gives the reactions for a thiocyanate; thus, with ferric chloride, an intense blood-red colour is produced, and with silver nitrate, a white precipitate, at first redissolving on shaking. Absence of thiocarbamide is shown by the fact that ammoniacal nitrate of silver throws down a white, curdy precipitate, which is not altered in colour even by boiling. Neither is the solution desulphurised by boiling with alkaline solution of lead.

A comparison of the properties of the substance described above with those of Paternò and Spica's "benzylthiocarbamide" leaves but little doubt that these chemists had in hand the isomeric benzylammonium thiocyanate. As already stated, their compound had a melting point of 101° and was very soluble in water; benzylammonium thiocyanate melts at 101—102° and is very soluble in the solvent named.

By the action of heat it is readily converted into the more stable benzylthiocarbamide; in this case, however, a comparatively high temperature is required to bring about the atomic re-arrangement; the non-observance of this condition doubtless accounts for Paternò and Spica's results.*

Action of Heat on Benzylammonium Thiocyanate.—A quantity of the pure thiocyanate was heated to a temperature of 150—160°. In about 15 minutes, the conversion was practically complete, a portion of the product giving with ferric chloride a comparative feeble reaction. The fused mass was now cooled, the solid product broken up, washed with cold water until the washings were free from thiocyanate, and the residue recrystallised from much boiling water.

The minute prisms which separated on cooling melted at 162°, and resembled in appearance, solubility, and reactions the product obtained from benzylthiocarbimide and ammonia. Proof of the identity was completed by a combustion for nitrogen:—

0·2150 gram, burnt with CuO and copper gauze in front, afforded 31·5 c.c. nitrogen, measured at 13° and 756·5 mm., or N = 17·22 per cent.

Calculated for $C_8H_{10}N_2S$, N = 16·90 per cent.

SECONDARY BENZYLATED THIOCARBAMIDES.

Orthotolylthiocarbimide and Benzylamine.—Benzylorthotolylthiocarbamide.

In order to prepare this compound, the base and thiocarbimide, each in somewhat dilute alcoholic solution, were mixed in the proportions required by the equation

$$CH_3\cdot C_6H_4\cdot NCS + C_6H_5\cdot CH_2\cdot NH_2 = CS<^{NH\cdot CH_2\cdot C_6H_5}_{NH\cdot C_6H_4\cdot CH_3}.$$

The mixture at once became warm, and the action was completed by heating to near the boiling point. As the liquid cooled, tufts of prisms separated, until at last the vessel could be inverted without loss of its contents. After being drained on the filter-pump and washed with alcohol, the product was practically pure. The yield was almost quantitative. On recrystallisation from boiling alcohol, the substance came down in tufts of white, rhombic prisms melting at 138—139° (uncorr.) without decomposition. The dry compound, when powdered, becomes very strongly electrical on friction with a spatula.

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* It is recorded by de Clermont (*Compt. rend.*, 1877, 351) that ethylamine hydrochloride and potassium thiocyanate, when boiled together in aqueous solution, evaporated to dryness, and heated for some time at 100°, yielded no ethylthiocarbamide; nor did ethylamine thiocyanate undergo this transformation, even when heated in a sealed tube at 150°. With amylamine under like conditions, no better results were obtained.

The formula was checked by a sulphur determination:—*

0·2630 gram, dried over sulphuric acid, afforded 0·2362 gram $BaSO_4$, or S = 12·34 per cent.
Calculated for $C_{15}H_{16}N_2S$, S = 12·51 per cent.

Benzylorthotolylthiocarbamide is not sensibly soluble in water even at the boiling temperature; it is only moderately soluble in boiling alcohol, and sparingly in cold.

Ammoniacal nitrate of silver produces in the alcoholic solution a whitish precipitate, changing almost at once to black. It is desulphurised slowly, owing, perhaps, to its insolubility, by boiling with alkaline solution of lead, a brilliant speculum being formed.

The preparation was now repeated, starting, however, from benzylthiocarbimide and orthotoluidine. The crystals thus obtained were undistinguishable in form and appearance from those produced by the combination of orthotolylthiocarbimide and benzylamine; they became electrical on friction, melted at the same temperature, namely, 138—139° (uncorr.), and, in short, behaved in all respects exactly like the latter.

Benzylthiocarbimide and Metatoluidine.—Benzylmetatolylthiocarbamide.

This substance was obtained by mixing the theoretical quantities of benzylthiocarbimide and metatoluidine, each in alcoholic solution. No sensible evolution of heat occurred, but the mixture, after being boiled, lost its cress-like odour, indicating that combination had taken place. On standing for some time, beautiful, vitreous, clear rhombs began to form; when the separation was completed, the latter were collected and washed with alcohol. The yield amounted to 82 per cent. of the theoretical, and the product was apparently quite pure, as its melting point was unaltered by recrystallisation from alcohol.

A sulphur determination, made with the recrystallised substance. gave the following result:—

0·2603 gram, dried in a vacuum over sulphuric acid, afforded 0·2314 gram $BaSO_4$, or S = 12·22 per cent.
Calculated for $C_{15}H_{16}N_2S$, S = 12·51 per cent.

---

* These sulphur determinations, except where otherwise specified, were made by Professor Emerson Reynolds' method, viz., evaporation to dryness in a nickel crucible with pure sodium hydroxide, and subsequent fusion of the product with potassium nitrate.

The interaction is similar to the preceding.

Benzylmetatolylthiocarbamide melts at 113—114° (uncorr.) without decomposition to a colourless liquid. It is almost insoluble in boiling water, and quite insoluble in cold. In boiling alcohol it dissolves tolerably freely, much more sparingly in cold; it is soluble also in ether, and freely so in chloroform.

The solution in alcohol is blackened at once on the addition of ammoniacal silver nitrate; and the sulphur is removed by boiling alkaline lead solution with formation of a brilliant mirror.

Benzylthiocarbimide and Paratoluidine.—Benzylparatolylthiocarbamide.

The base and thiocarbimide, in molecular proportion, were mixed in alcoholic solution; the substances combined with evolution of heat, and the action was completed by further warming. In about an hour, the separation of solid matter commenced; when this was at an end, the product was drained on the filter-pump and washed with alcohol. As in the preceding case, the substance was practically pure; the yield amounted to 88 per cent. of the theoretical.

On recrystallisation from boiling alcohol, the thiocarbamide came down in fine, large, vitreous, clear, rhombic crystals, which were dried over sulphuric acid in a vacuum.

A sulphur estimation gave the following result:—

0·3044 gram yielded 0·2764 gram $BaSO_4$, or S = 12·48 per cent.
Calculated for $C_{15}H_{16}N_2S$, S = 12·51 per cent.

The action is formulated as before.

Benzylparatolylthiocarbamide melts at 120—121° (uncorr.) to a colourless liquid; its melting point thus stands intermediate between those of the meta- and ortho-compounds, which are 114° and 139° respectively. It is extremely sparingly soluble in boiling water, insoluble in cold, freely in boiling alcohol, much less so in cold. It dissolves readily in chloroform, moderately in ether and benzene, but is insoluble in light petroleum, which precipitates it from the last-named solvent in minute, rhombic prisms.

Ammoniacal silver nitrate at once withdraws the sulphur from the cold alcoholic solution, and the substance is also attacked, with formation of a fine speculum, by boiling alkaline solution of lead.

Benzylthiocarbimide and Metaxylidine.—Benzylmetaxylylthiocarbamide.

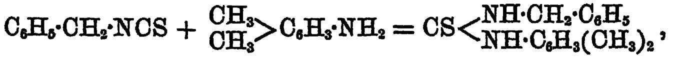
Alcoholic solutions were mixed, containing benzylthiocarbimide and metaxylidine in molecular proportion. No heat was evolved; the mixture was therefore boiled for a short time and set aside. After standing for about 24 hours, the solution, on shaking, began to deposit crystals; the latter, which were white and waxy-looking, formed rapidly, and grew to a considerable size. On recrystallisation from boiling alcohol, the substance was obtained in very fine, large, colourless, apparently monoclinic prisms melting at 84—85° (uncorr.).

A sulphur determination showed that the expected thiocarbamide had been produced:—

0·2683 gram, dried in a vacuum over sulphuric acid, afforded 0·2277 gram $BaSO_4$, or $S = 11{\cdot}66$ per cent.

Calculated for $C_{16}H_{18}N_2S$, $S = 11{\cdot}86$ per cent.

The action is thus expressed:—



$$C_6H_5{\cdot}CH_2{\cdot}NCS + \begin{matrix}CH_3\\CH_3\end{matrix}{>}C_6H_3{\cdot}NH_2 = CS{<}\begin{matrix}NH{\cdot}CH_2{\cdot}C_6H_5\\NH{\cdot}C_6H_3(CH_3)_2\end{matrix},$$

and the yield amounted to about 90 per cent. of the theoretical.

When heated with water, the substance melts and dissolves to a slight extent; on cooling, the solution becomes milky-looking from separation of minute, oily globules. It is extremely soluble in boiling alcohol, much less so in cold, soluble in ether, and freely so in chloroform. The aqueous solution is desulphurised slowly and imperfectly by boiling with alkaline lead solution.

Benzylthiocarbimide and α-Naphthylamine.—Benzyl-α-naphthylthiocarbamide.

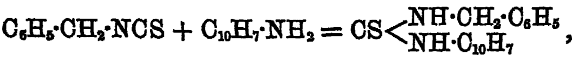
To prepare this compound, the base and thiocarbimide in molecular proportion were mixed in alcohol, and the solution heated to boiling. The odour of both constituents soon ceased to be noticeable, and, on cooling, crystals separated, which were collected, drained on the filter-pump, and washed with alcohol. On recrystallisation from the same solvent, colourless rhombs were obtained, having a micaceous lustre and melting at 172—173° (uncorr.) to a colourless liquid.

The formula was checked by a nitrogen determination:—

0·2248 gram, burnt with CuO and copper gauze in front, afforded 18·5 c.c. gas, measured at 18° and 767 mm., or $N = 9{\cdot}65$ per cent.

Calculated for $C_{18}H_{16}N_2S$, $N = 9{\cdot}61$ per cent.

The action takes place according to the equation



$$C_6H_5{\cdot}CH_2{\cdot}NCS + C_{10}H_7{\cdot}NH_2 = CS{<}\begin{matrix}NH{\cdot}CH_2{\cdot}C_6H_5\\NH{\cdot}C_{10}H_7\end{matrix},$$

and the yield amounted to over 93 per cent. of the theoretical.

Benzyl-α-naphthylthiocarbamide dissolves sparingly in hot alcohol, and still less in cold; it is almost insoluble in ether, moderately soluble in chloroform. Benzene dissolves it sparingly, whilst light petroleum, in which it is insoluble, precipitates it from the last solvent in microscopic, pointed prisms.

Silver nitrate, when added to the alcoholic solution, throws down an amorphous, white precipitate; this rapidly changes colour, darkening, and finally becoming, even in the cold, quite black. The ammoniacal nitrate blackens the solution instantly; and the sulphur is also readily removed by boiling with alkaline lead solution, the sides of the tube becoming brilliantly plated.

Benzylthiocarbimide and β-Naphthylamine.—Benzyl-β-naphthylthiocarbamide.

The constituents in molecular proportion were boiled together for a short time in alcoholic solution. The odour of benzylthiocarbimide gradually diminished; on cooling, solid matter separated freely. This was drained from the crimson mother liquor by means of the filter-pump, well washed with spirit, and recrystallised from much boiling alcohol. The product, consisting of clear, colourless, micaceous, rhombic plates, was dried over sulphuric acid in a vacuum, and the sulphur estimated:—

0·2850 gram afforded 0·2222 gram $BaSO_4$, or $S = 10·72$ per cent.
Calculated for $C_{18}H_{16}N_2S$, $S = 10·97$ per cent.

The equation expressing the action is formulated as in the preceding case; the yield, a little over 93 per cent., was identical with that of the α-compound.

Benzyl-β-naphthylthiocarbamide melts at 165—166° (uncorr.) to a colourless liquid, that is, 7° lower than its metamer. It is insoluble in water, either hot or cold; sparingly soluble in boiling alcohol, still less so in cold. It is soluble also in ether, chloroform, and benzene, separating from the last-named solvent in the form of a white, flocculent, microcrystalline powder.

Silver nitrate, added to the alcoholic solution, gives a yellowish-white, finely-divided, amorphous precipitate, which slowly darkens; with ammoniacal silver nitrate, a black precipitate falls at once. On boiling with alkaline lead solution, the sulphur is moderately readily removed, and the sides of the tube become plated with a very brilliant galena mirror.

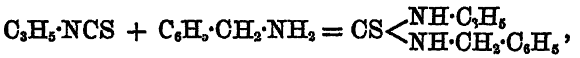
Allylthiocarbimide and Benzylamine.—Allylbenzylthiocarbamide.

This compound was prepared by mixing the theoretical quantities of the constituents in alcoholic solution. Vigorous combination occurred, the heat evolved being sufficient to boil off a portion of the alcohol; on cooling, brilliant crystals separated, which were removed, washed well with cold, and recrystallised from boiling, alcohol. The substance was thus obtained in brilliant, colourless, rhombic crystals, which were dried over sulphuric acid for analysis.

Evaporation with aqueous or alcoholic sodium hydroxide incompletely removes the sulphur from this compound; the sulphur determinations hence fell from 1 to 3 per cent. too low; a preliminary heating with nitric acid, however, met the difficulty.

0·2762 gram afforded 0·3108 gram $BaSO_4$, or $S = 15·47$ per cent.
Calculated for $C_{11}H_{14}N_2S$, $S = 15·54$ per cent.

The interaction runs thus:—



$$C_3H_5\cdot NCS + C_6H_5\cdot CH_2\cdot NH_2 = CS{<}\begin{matrix}NH\cdot C_3H_5\\ NH\cdot CH_2\cdot C_6H_5\end{matrix},$$

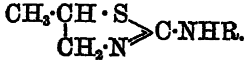
and the yield amounted to nearly 90 per cent. of the theoretical.

Allylbenzylthiocarbamide melts between 93 and 94° (uncorr.) to a colourless liquid. When heated with water, it dissolves to a trifling extent; on cooling, the solution becomes milky from separation of a cloud of minute oily globules, which, after standing for a short time, solidify to microscopic crystals. It is rather freely soluble in hot alcohol, moderately in cold; soluble in ether, and very freely in chloroform.

Ammoniacal silver nitrate, when added to the cold alcoholic solution, immediately precipitates silver sulphide; but the sulphur is removed by alkaline lead solution imperfectly, and only after prolonged boiling, a galena speculum being produced.

Action of Hydrochloric Acid upon Allylbenzylthiocarbamide.—Benzylpropylene-ψ-thiocarbamide.

Gabriel has shown (*Ber.*, **22**, 2984) that allylthiocarbamide, when heated with fuming hydrochloric acid, undergoes intramolecular change, yielding an isomeric base. This process has been extended by Prager (*Ber.*, **22**, 2991) to the aromatic, and by Avenarius (*ibid.*, **24**, 260) to the alkyl-substitution, derivatives of allylthiocarbamide; the result of their investigations showing that the behaviour is general for the allylthiocarbamides, and that the product of the change is a compound of the form



$$\begin{matrix}CH_3\cdot CH\cdot S\\ |\quad\quad\\ CH_2\cdot N\end{matrix}{>}C\cdot NHR.$$

On treating benzylthiosinamine according to Gabriel's method, the following results were obtained:—

A quantity of the thiocarbamide was sealed up with three times its own weight of fuming hydrochloric acid, and the mixture kept for two hours at a temperature of about 100°. There was no pressure on opening the tube, and its contents, when concentrated to a small bulk, formed a colourless, syrupy liquid, which showed no tendency to crystallise.

This liquid, when treated with excess of aqueous potash, deposited a heavy oil, which, shortly after removal, solidified. The product was well washed with cold water, dissolved in warm alcohol, and the solution precipitated by pouring into water. A colourless, heavy oil separated; when this solidified, it was broken up, drained, washed, and dried. A portion was further purified by dissolving it in boiling water, and shaking the solution until cool; by this treatment the substance was obtained in fine, white needles, melting at 65—66° without decomposition.

A nitrogen determination gave the following result:—

0·2164 gram burnt with CuO and copper gauze in front, afforded 25·5 c.c. of gas, measured at 11·5° and 759 mm., or $N = 13{\cdot}99$ per cent.

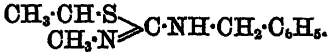
Calculated for $C_{11}H_{14}N_2S$, $N = 13{\cdot}62$ per cent.

The solution has a strongly alkaline reaction to test-paper, but the substance is too sparingly soluble in water to admit of a direct determination of its alkalinity by titration. This was effected, however, by dissolving in excess of standard acid, and titrating back by alkali:—

0·2979 gram neutralised 14·7 c.c. N/10 HCl, or HCl combined in hydrochloride = 15·21 per cent.

Calculated for $C_{11}H_{14}N_2S,HCl$, $HCl = 15{\cdot}02$ per cent.

The substance is accordingly " benzylpropylene-ψ-thiocarbamide."



$$\left.\begin{array}{r}CH_3{\cdot}CH{\cdot}S\\ CH_3{\cdot}N\end{array}\right> C{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5.$$

It has a faint unpleasant smell, which becomes more pronounced on warming. It is sparingly soluble in boiling water, almost insoluble in cold; very freely soluble in alcohol, ether, chloroform and benzene; and moderately so in light petroleum, separating from the latter in tufts of vitreous prisms. Dilute mineral acids readily dissolve the substance, which is precipitated at once, as an oil, from the acid solution, by alkalis or ammonia.

The alcoholic solution gives no colour-change with ferric chloride; ammoniacal silver nitrate produces a white, milky-looking precipitate, not perceptibly altered by heating; the sulphur, moreover, is not withdrawn by even prolonged boiling with alkaline solution of lead.

Acetylthiocarbimide and Benzylamine.—Acetylbenzylthiocarbamide.

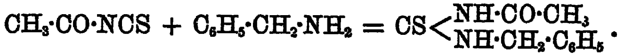
To prepare this compound, acetylthiocarbimide, dissolved in well-cooled benzene, was gradually added in molecular proportion to pure benzylamine, also dissolved in a considerable volume of benzene, and cooled to near the freezing point. The liquid became reddish, and the penetrating odour of the thiocarbimide soon ceased to be perceptible. After evaporation of the benzene, a viscid liquid remained, from which a quantity of a yellow solid slowly deposited. The latter was collected on the vacuum-pump, washed well with cold spirit, and recrystallised from alcohol. It was still yellowish, but, after another recrystallisation, was obtained in long, thin, pearly plates, free from colour, and melting at 128—129° (uncorr.).

The yield is very poor; on operating in ethereal solution, no solid substance could be obtained. Even when using benzene, unless the solutions are much diluted and well cooled, the action becomes violent, and the product is a tarry or syrupy mass, which refuses to crystallise.

A portion of the recrystallised substance was dried over sulphuric acid in a vacuum, and the sulphur estimated, with the following result:—

0·2554 gram afforded 0·2906 gram $BaSO_4$, or $S = 15·64$ per cent.
Calculated for $C_{10}H_{12}N_2SO_2$, $S = 15·40$ per cent.

The product is, therefore, acetylbenzylthiocarbamide, formed according to the equation



$$CH_3·CO·NCS + C_6H_5·CH_2·NH_2 = CS{<}\begin{matrix}NH·CO·CH_3\\NH·CH_2·C_6H_5\end{matrix}.$$

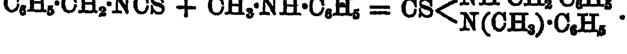
It is insoluble in water; moderately soluble in cold alcohol, freely in hot; soluble in ether and freely in chloroform.

The alcoholic solution gives no colour with ferric chloride; it is readily desulphurised by boiling with alkaline solution of lead. With ammoniacal silver nitrate, a whitish precipitate falls, which blackens immediately.

TERTIARY BENZYLATED THIOCARBAMIDES.

Benzylthiocarbimide and Methylaniline.—Benzylmethylphenylthiocarbamide.

Benzylthiocarbimide was added to methylaniline and a little alcohol in the proportion required by the equation



$$C_6H_5·CH_2·NCS + CH_3·NH·C_6H_5 = CS{<}\begin{matrix}NH·CH_2·C_6H_5\\N(CH_3)·C_6H_5\end{matrix}.$$

The mixture gradually became hot, indicating that union had occurred, but, after cooling, remained clear; the addition of a few crystals obtained from a previous qualitative experiment at once determined the crystallisation of the product. This was dissolved in boiling alcohol; on cooling, beautiful, large, white prisms separated, which were drained on the filter-pump, washed slightly with spirit, and dried in a vacuum over sulphuric acid. The quantity of substance thus obtained amounted to over 94 per cent. of the weight of materials employed.

A nitrogen determination gave the following result:—

0·2081 gram, burnt with CuO and copper gauze in front, afforded 20·2 c.c. nitrogen, measured at 17° and 757 mm., or N = 11·21 per cent.

Calculated for $C_{15}H_{16}N_2S$, N = 10·97 per cent.

When heated in a narrow tube, the benzylmethylphenylthiocarbamide melted at 84—85° (uncorr.).

On warming with water, it melts to a yellowish, oily liquid, which dissolves slightly; on cooling again, the dissolved substance separates as a white, milky-looking cloud of minute droplets. It is very freely soluble in hot alcohol, sparingly in cold; soluble in ether, and freely so in chloroform, on which it floats; it is soluble also in benzene, and moderately so in light petroleum.

Neither the aqueous nor the alcoholic solution is desulphurised by treatment with alkaline solution of lead. Silver nitrate, when added to the alcoholic solution, causes no precipitate; the ammoniacal nitrate, on the other hand, throws down a white, curdy precipitate, which dissolves when the liquid is warmed; the clear solution, on boiling, is rapidly decomposed, and a dull-black coating forms on the sides of the containing tube.

It is now clearly established* that a given thiocarbimide, X·NCS, when combined with a given primary amine, Y·NH_2, yields a compound identical with that produced from the thiocarbimide Y·NCS and the amine X·NH_2; Hecht (*Ber.*, 23, 288) instances this still further, and uses the fact as an argument for the symmetrical structure of the disubstituted thiocarbamides thus obtained. But, though a number of tertiary thiocarbamides have been prepared, by Mainzer, Gebhardt, and others, by the union of thiocarbimides with secondary amines, no attempt appears to have been made, as yet, to ascertain whether isomeric or identical forms would result from combinations where certain groups in thiocarbimide and secondary amine, respectively, are transposed. I have, therefore, taken this opportunity to prepare a few such compounds, with the results detailed below.

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* See, *e.g.*, Weith, *Ber.*, 8, 1523 and 1529.

Methylthiocarbimide and Benzylamine.—Methylphenylbenzylthiocarbamide.

The base and thiocarbimide in molecular proportion were mixed in alcoholic solution, the mixture boiled and set aside. After several days' standing, the combination of the constituents was complete, and a crystalline mass had separated; this, after draining on the filter-pump, washing with spirit, and drying, amounted to over 91 per cent. of the weight of the materials used.

On recrystallisation from boiling alcohol, the substance came down in tufts of long, shining, white prisms, which, when pressed and dried, melted between 120° and 121° without decomposition.

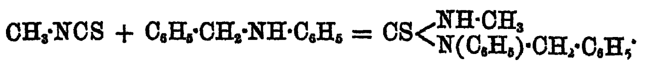
A sulphur determination gave the following result:—

0·3834 gram, oxidised with nitric acid, and treated with NaOH + KNO_3, afforded 0 3630 gram $BaSO_4$, or $S = 13{\cdot}01$ per cent.
Calculated for $C_{15}H_{16}N_2S$, $S = 12{\cdot}51$ per cent.

The substance is very sparingly soluble in boiling water, insoluble in cold. It dissolves readily in boiling alcohol, much more sparingly in cold, freely in ether, very freely in chloroform, moderately in carbon bisulphide and benzene, and somewhat sparingly in light petroleum.

Even after prolonged boiling with alkaline solution of lead, the mixture remains colourless. Silver nitrate, when added to the alcoholic solution, produces no precipitate, but the mixture slowly darkens. With ammoniacal nitrate of silver, a yellowish-white precipitate falls; this is stable in the cold, but, on heating, becomes first orange-red, then black, and a mirror gradually forms.

In appearance, to some extent, and in general properties, this and the preceding compound resemble one another somewhat closely, but the remarkable difference between their melting points, 36°, at once characterises them as isomeric. The action in the latter case may therefore be written—



$$CH_3{\cdot}NCS + C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}C_6H_5 = CS\begin{smallmatrix}\diagup NH{\cdot}CH_3 \\ \diagdown N(C_6H_5){\cdot}CH_2{\cdot}C_6H_5.\end{smallmatrix}$$

In the pair of compounds next to be described the general resemblance is strikingly close.

Benzylthiocarbimide and Ethylaniline.—Benzylethylphenylthiocarbamide.

This compound was prepared by mixing the theoretical quantities of base and thiocarbimide. The mixture became slightly warm, but, after standing for some days, combination was found to be still incomplete; the contents of the vessel were therefore heated to boiling, and set aside. After two days, the clear, oily liquid was surrounded by a freezing mixture, under which treatment crystallisation commenced in about an hour. When complete, the mother liquor was drained from the pulpy mass by means of the filter-pump, the white residue well washed with cold spirit, and finally recrystallised from boiling alcohol.

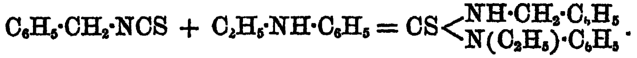
From this solvent, the substance was deposited in the form of long, slender, oblique prisms, grouped in rosettes, and melting at 90—91° (uncorr.).

A portion, dried over sulphuric acid, gave the following results on analysis:—

0·2629 gram, burnt with CuO and copper gauze in front, afforded 24·5 c.c. nitrogen, measured at 18° and 756 mm., or $N = 10{\cdot}70$ per cent.

Calculated for $C_{16}H_{18}N_2S$, $N = 10{\cdot}40$ per cent.

The substance is accordingly benzylethylphenylthiocarbamide; its formation may be thus represented:—



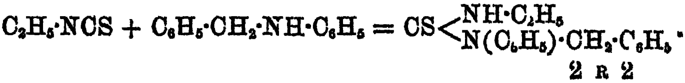
$$C_6H_5{\cdot}CH_2{\cdot}NCS + C_2H_5{\cdot}NH{\cdot}C_6H_5 = CS{<}\begin{matrix}NH{\cdot}CH_2{\cdot}C_6H_5\\N(C_2H_5){\cdot}C_6H_5\end{matrix}.$$

When heated with water, it melts and dissolves to a trifling extent, separating again, as the solution cools, as a cloud of minute, oily globules. It is almost indefinitely soluble in boiling alcohol, only moderately so in cold; and dissolves freely in ether, chloroform, and benzene; the latter solution is not precipitated by light petroleum.

Like the other tertiary thiocarbamides, it is not desulphurised by boiling with alkaline solution of lead. Silver nitrate, when added to the alcoholic solution, fails to cause a precipitate; but the mixture, even in the cold, soon begins to decompose; it becomes first grey, then black, and after a little time a speculum forms on the sides of the tube. With ammoniacal silver nitrate, a curdy, white precipitate is produced; this, on heating, first becomes yellow and seems to partially dissolve; the liquid then rapidly blackens, and a speculum appears.

Ethylthiocarbimide and Benzylaniline.—Ethyl-benzylphenylthiocarbamide.

The secondary base and thiocarbimide were mixed, in concentrated alcoholic solution, in the proportions required by the equation



$$C_2H_5{\cdot}NCS + C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}C_6H_5 = CS{<}\begin{matrix}NH{\cdot}C_2H_5\\N(C_6H_5){\cdot}CH_2{\cdot}C_6H_5\end{matrix}.$$

No heat was evolved, and after boiling and letting stand for a day the liquid still smelt pungently of the mustard oil; it was therefor sealed up and heated for about two hours at 100°, by which mean the desired combination was effected. The contents of the tub solidified at once on removal, the yield of solid product amounting t nearly 80 per cent. of the theoretical.

By recrystallisation from alcohol, the substance was obtained i colourless, short, thick, rectangular prisms, possessing a rathe greasy lustre, and melting between 90·5° and 91° (uncorr.).

Analysis of a portion, dried over sulphuric acid, gave the followin result:—

0·2019 gram, burnt with CuO and copper gauze in front, afforde 17·6 c.c. nitrogen, measured at 13·5° and 775 mm., or N = 10·4 per cent.

Calculated for $C_{16}H_{18}N_2S$, N = 10·40 per cent.

Ethyl-benzylphenylthiocarbamide is insoluble in cold water, an very sparingly soluble at the boiling temperature. It dissolve almost indefinitely in boiling alcohol, moderately in cold; readil in ether and benzene, and is not precipitated from the last-name solvent by light petroleum.

Alkaline lead solution fails, even on prolonged boiling, to remov the sulphur. Silver nitrate, when added to the alcoholic solution causes no precipitate; but the liquid slowly changes in colour becoming first clear yellow, then reddish, and finally almost black No speculum is formed. With ammoniacal nitrate of silver, a white curdy precipitate falls, which, on heating, at once blackens, with production of a mirror. Both this and the preceding compounds giv white, curdy, mercurial derivatives on treatment with mercuri chloride.

On comparing the properties of the substance in question with tha of the isomer preceding, a very close resemblance is noticeable Their melting points are practically the same; there is no substantial difference as regards the action of the common solvents; the agree in the resistance which they offer to the removal of thei sulphur by alkaline lead solution, and in some other respects. Th differences in their behaviour with ammoniacal and ordinary silve nitrate, though perceptible, are by no means striking; and, save fo the difference in their crystalline forms, they might easily pass fo identical.

The idea did, in fact, suggest itself that the comparatively hig temperature to which the constituents had been subjected in th latter case might possibly have determined a position-change in th substituting groups. This suspicion was experimentally tested by gently warming an alcoholic solution of ethylthiocarbimide with benzylaniline in molecular proportion, and allowing the mixture to stand in the cold until combination, which gradually took place, was complete. The solid product thus obtained, when purified by recrystallisation from alcohol, formed rectangular prisms, melting at the same temperature as, and undistinguishable from, those prepared from the same constituents under pressure.

Whether or not these compounds are really isomeric can scarcely be decided on the data recorded. Analogy with the methyl-phenyl-benzyl derivative and its isomer would suggest an affirmative answer; but, on the other hand, the difference in crystalline form may be explicable on other grounds, and, moreover, it seems strange that the transposition of the *ethyl* and benzyl groups should fail to affect the melting point, when it is observed how greatly this is influenced when *methyl* and benzyl change places.

Provisionally, they may be regarded as position-isomers. As, however, the present paper is concerned chiefly with the description of benzylic derivatives of thiocarbamide, the question of isomerism in this and some other like cases may be reserved for a future communication.

Benzylthiocarbimide and Benzylaniline.—Benzyl-phenylbenzylthiocarbamide.

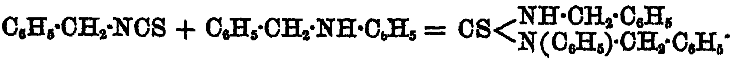
In order to prepare this substance, benzylthiocarbimide was mixed with an alcoholic solution containing molecular proportions of benzylaniline, dissolved in a little hot alcohol. On cooling, oily droplets separated, which, after standing for some hours, solidified to a crystalline mass; by crystallisation from alcohol, the substance was obtained in the form of white, pointed prisms melting between 102° and 103° (uncorr.).

A nitrogen determination showed that the expected dibenzylphenylthiocarbamide had been produced:—

0·2218 gram, burnt with CuO and copper gauze in front, afforded 17 c.c. of gas, measured at 17·5° and 752 mm., or N = 8·77 per cent.

Calculated for $C_{21}H_{20}N_2S$, N = 8·45 per cent.

The action is thus formulated:—



$$C_6H_5{\cdot}CH_2{\cdot}NCS + C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}C_6H_5 = CS{<}\begin{matrix}NH{\cdot}CH_2{\cdot}C_6H_5\\ N(C_6H_5){\cdot}CH_2{\cdot}C_6H_5\end{matrix}.$$

On heating with water, the substance melts readily, but does not sensibly dissolve, even at the boiling point. It is freely soluble in alcohol, ether, chloroform, and benzene; and dissolves also, though somewhat sparingly, in light petroleum, separating from the last-named solvent in minute, very brilliant, short prisms.

Like its congeners already described, it is not desulphurised by boiling with alkaline lead solution. Ammoniacal silver nitrate, when added to a cold alcoholic solution, throws down a curdy, white precipitate, which, on boiling, is slowly blackened, with formation of a speculum of silver sulphide.

Benzylthiocarbimide and Piperidine.—Benzylpiperidylthiocarbamide.

To prepare this substance, piperidine was added to an alcoholic solution of benzylthiocarbimide in the proportions indicated by the equation

$$C_6H_5{\cdot}CH_2{\cdot}NCS + C_5H_{10}{:}NH = CS\left<\begin{array}{l}NH{\cdot}CH_2{\cdot}C_6H_5\\ N{:}C_5H_{10}\end{array}\right. .$$

Heat was evolved sufficient to boil off a portion of the alcohol, and the combination was completed by boiling for a short time. The mixture, on cooling, solidified to a radiating crystalline mass, which was pressed between folds of bibulous paper, and recrystallised from spirit. Rosettes of large, white, waxy-looking prisms were thus obtained which, when dried, melted at 87—88° (uncorr.).

A portion was oxidised by heating with concentrated nitric acid, and the sulphur determined:—

0·4009 gram afforded 0·3988 gram $BaSO_4$, or $S = 13·67$ per cent.

0·2343 gram, burnt with CuO and copper gauze in front, gave 24·5 c.c. nitrogen, measured at 13·5° and 763 mm., or $N = 12·37$ per cent.

	Calculated for $C_{13}H_{18}N_2S$.	Experiment.
S	13·69	13·67
N	11·99	12·37

Benzylpiperidylthiocarbamide is slightly soluble in boiling water; as the solution cools, a cloud of minute droplets separates, which, in a short time, solidify to colourless, hair-like needles. It dissolves very freely in boiling alcohol, moderately in cold; easily in chloroform, ether, benzene, and carbon bisulphide. Light petroleum dissolves it moderately when hot, sparingly in the cold. It is also soluble in concentrated hydrochloric acid, and separates, on dilution with water, in the form of oily drops, which soon change to fine needles.

As a tertiary derivative of thiocarbamide, this substance withholds its sulphur from alkaline lead solution, even though the boiling be prolonged. Ammoniacal nitrate of silver, as a general rule, desulphurises the tertiary thiocarbamides less readily than the neutral nitrate; here also this is the case. A cold alcoholic solution, if mixed with the ordinary nitrate, begins to darken almost at once, and gradually becomes quite black; if, on the other hand, the ammoniacal nitrate be added, the solution remains colourless for days. On warming the mixture, silver sulphide at once separates.

The alcoholic solution gives, with ferric chloride, a deep-yellow coloration, changing, on warming, to a clear mahogany-brown. With copper sulphate, a rich, deep-purple colour is produced which, on the addition of water, disappears, leaving the mixture white and turbid.

Cold sulphuric acid dissolves the substance; after standing for a short time, the solution becomes white and milky-looking. If the mixture be now warmed it clears, with production of a grass-green coloration; on further heating, the contents of the vessel become black and carbonised.

Chemical Laboratory, Queen's College, Galway.

LII.—*Ethyl αα'-Dimethyl-αα'-diacetylpimelate and its Decomposition Products.*

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WITH the exception of the compounds recently described by W. H. Perkin, jun., and one of us (Trans., this vol., p. 214), no derivatives of heptamethylene, whose constitution has been proved experimentally, have yet been prepared; the compounds referred to were obtained from αα'-diacetylpentane, this substance, on reduction, being converted into dimethyldihydroxyheptamethylene.

As it seemed probable that other 1:7-diketones would behave in a similar manner, we have prepared αα'-dimethyldiacetylpentane; experiments on the reduction of this diketone are being carried out by one of us, but, as some time must elapse before the investigation is completed, we describe in this paper various compounds which have been obtained in studying the preparation of dimethyldiacetylpentane.

The following summary of our results may, perhaps, advantageously precede the detailed description of the experiments:—

Ethyl αα'-dimethyl-αα'-diacetylpimelate, $C_{17}H_{28}O_6$, is obtained in considerable quantities when ethyl methylacetoacetate (2 mols.) is treated with sodium ethoxide (2 mols.) and trimethylene bromide (1 mol.) in absolute alcoholic solution; its formation is represented by the equation

$$2CH_3{\cdot}CO{\cdot}CNaMe{\cdot}COOEt + C_3H_6Br_2 = \\ COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 2NaBr.$$

It is a colourless, moderately thick liquid, boiling at 233—235° under a pressure of 50 mm.; that it has the constitution expressed by the formula given above is shown (1) by its method of formation, (2) by the study of its decomposition products, and (3) by the fact that it combines with phenylhydrazine (2 mols.), yielding a *dihydrazone* of the composition $C_{29}H_{40}N_4O_4$.

When ethyl dimethyldiacetylpimelate is hydrolysed with alkalis, it yields dimethylpimelic acid, dimethylacetylcaproic acid, and dimethyldiacetylpentane, according to the equations

$$\text{I. } COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 4KOH = \\ COOK{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOK + 2C_2H_3O_2K + 2C_2H_5{\cdot}OH.$$

$$\text{II. } COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 4KOH = \\ CHMeAc{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOK + C_2H_3O_2K + 2C_2H_5{\cdot}OH \\ + K_2CO_3.$$

$$\text{III. } COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 4KOH = \\ CHMeAc{\cdot}[CH_2]_3{\cdot}CHMeAc + 2K_2CO_3 + 2C_2H_5{\cdot}OH.$$

The relative yield of these three products depends greatly on the method of hydrolysis employed; under the most suitable conditions, the yield of pure dimethyldiacetylpentane is only about 12—13 per cent. of the crude ethereal salt.

αα′-Dimethylpimelic acid, $COOH{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOH$, crystallises from hot light petroleum in transparent twin prisms, melts at 80—81°, boils at 250—251° under a pressure of 53 mm., and is readily soluble in water and most ordinary organic solvents, except light petroleum. The *silver* salt, $C_9H_{14}O_4Ag_2$, *barium* salt, $C_9H_{14}O_4Ba$, and *ethyl* salt, $C_9H_{14}O_4Et_2$, are described.

αα′-Dimethylacetylcaproic acid, $CHMeAc{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOH$, is a colourless, odourless liquid, boiling at about 224° under a pressure of 63 mm.; it is hygroscopic, and is difficult to obtain in a state of purity. The *silver* salt, $C_{10}H_{17}O_3Ag$, *ethyl* salt, $C_{10}H_{17}O_3Et$, *methyl* salt, $C_{10}H_{17}O_3Me$, and the *oxime*, $C_{10}H_{19}NO_3$, were prepared.

αα′-Dimethyldiacetylpentane, $CH_3{\cdot}CO{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CO{\cdot}CH_3$, is a colourless liquid, boiling at 190—192° under a pressure of 100 mm.; it does not combine with sodium hydrogen sulphite, but when treated with hydroxylamine, it is converted into a crystalline dioxime, $C_{11}H_{22}N_2O_2$, which melts at 95—96°.

Ethyl $\alpha\alpha'$-dimethylpimelate, COOEt·CHMe·$[CH_2]_3$·CHMe·COOEt, is formed, in the place of ethyl dimethyldiacetylpimelate, when ethyl methylacetoacetate is treated with sodium ethoxide and trimethylene bromide in alcoholic solution, the alcohol employed being not quite anhydrous; it is a colourless liquid, boiling at 190—191° under a pressure of 80 mm., and, on hydrolysis, it yields an acid identical with the $\alpha\alpha'$-dimethylpimelic acid obtained from ethyl dimethyldiacetylpimelate.

Ethyl $\alpha\alpha'$-Dimethyldiacetylpimelate, COOEt·CMeAc·$[CH_2]_3$·CMeAc·COOEt.

The reaction which takes place between ethyl sodiomethylacetoacetate and trimethylene bromide in boiling alcoholic solution is a rather complicated one, for besides ethyl dimethyldiacetylpimelate, the formation of which can be expressed by the equation given above (p. 570), a considerable quantity of a mixture of compounds of lower boiling point is produced; the nature of this bye-product has not been definitely ascertained, but, in all probability, it consists of a mixture of ethyl methylallylacetoacetate with regenerated ethyl methylacetoacetate.

For the preparation of ethyl dimethyldiacetylpimelate, the following method is employed:—A mixture of trimethylene bromide (105 grams) and pure ethyl methylacetoacetate (144 grams) is poured, in small quantities at a time, into a large flask containing a cold solution of sodium (23 grams) in absolute alcohol (260—280 grams), the mixture being shaken well, and also cooled from time to time under the tap, so that no considerable rise of temperature occurs. By the time the whole of the mixture has been added, the contents of the flask have become almost completely solid, owing to the formation of ethyl sodiomethylacetoacetate; it is for this reason that it is advisable to mix the ethyl methylacetoacetate with the trimethylene bromide, instead of adding the two compounds to the sodium ethoxide consecutively, as, when the latter course is adopted, the solid mass of ethyl sodiomethylacetoacetate is only slowly acted on.

The mixture is then gradually heated to boiling on the water-bath; the solid sodium derivative gradually crumbles away, sodium bromide is precipitated, and after heating from one to two hours the reaction is usually at an end, the solution then showing a neutral reaction. After distilling off the alcohol as completely as possible in a salt-bath, and adding a small quantity of water to dissolve the sodium bromide, the oily product is separated from the aqueous solution with the aid of a funnel, the residue extracted once with ether, and the ethereal extract mixed with the main portion of the oil; this solution is washed with dilute sulphuric acid, then twice with water, dried over calcium chloride, filtered, and the ether evaporated. The residue consists of a yellowish oil, the weight of which is usually about 150 grams; it is a mixture of various compounds, from which the ethyl dimethyldiacetylpimelate can be isolated either by submitting the mixture to distillation with steam, or by fractional distillation under reduced pressure.

When the former method is adopted, a large quantity of an almost colourless oil collects in the receiver, the non-volatile ethyl dimethyldiacetylpimelate remaining as a thick, yellow oil, which can be easily separated with the aid of a funnel; the weight of the dried, impure compound obtained in this way is about one-half that of the original oil, namely, about 70 grams from 144 grams of ethyl methylacetoacetate. On distillation, under reduced pressure (60 mm.), it begins to boil at about 210°, the thermometer rising pretty quickly to 240°, the principal portion passing over between 240° and 260°; the pure compound can be easily isolated from the highest boiling fraction by redistilling once or twice under reduced pressure.

The second method which can be employed for isolating the ethyl dimethyldiacetylpimelate is, perhaps, the more convenient of the two; in this case the crude product is fractionally distilled under reduced pressure without first separating the compounds which are volatile with steam. The quantities of the various fractions obtained from the original oil at the first distillation are as follows:—

Crude product		226 grams.	Crude product		105 grams.
Pressure		80 mm.	Pressure		60 mm.
Fraction	100—185°	103 grams.	Fraction	110—160°	40 grams.
„	185—200	15 „	„	160—210	10 „
„	200—270	104 „	„	210—250	50 „
Trace of residue.			Slight residue.		

The first fraction, in both cases, has doubtless the same composition as the oil which passes over on distillation with steam; the intermediate fraction is a mixture of various compounds, and is added to the crude product from a subsequent operation; the third fraction consists almost entirely of ethyl dimethyldiacetylpimelate, and is employed without further purification for the preparation of dimethyldiacetylpentane; the quantity of this impure product is, on the average, about 50 per cent. of the original oil.

Ethyl dimethyldiacetylpimelate can be easily obtained in a pure condition by fractionating the impure liquid once or twice under reduced pressure; the following are analyses of two different samples of the compound:—

I. Fraction boiling at 237—242°, under a pressure of 60 mm., 0·1897 gram substance gave 0·4314 gram CO_2 and 0·1498 gram H_2O.

II. Fraction boiling at 233—235°, under a pressure of 50 mm., 0·1845 gram substance gave 0·4205 gram CO_2 and 0·1445 gram H_2O.

	Calculated for	Found.	
		I.	II.
C........	62·19 per cent.	62·02	62·15 per cent.
H........	8·53 „	8·77	8·70 „
O........	29·28 „	29·21	29·15 „

Ethyl dimethyldiacetylpimelate is a colourless, moderately thick liquid with a slight pleasant, aromatic odour, but its vapours are pungent and irritating; it boils at 233—235° under a pressure of 50 mm., at about 248—252° under a pressure of 80 mm., and when heated in small quantities it boils without any noticeable decomposition under the ordinary atmospheric pressure. It shows no signs of crystallising even when kept at 0° for some time, and it is not volatile with steam; it is specifically heavier than, and insoluble in, cold water, but it dissolves to a slight extent in hot water, separating again from the solution on cooling. It is miscible with alcohol, ether, &c., in all proportions, and it dissolves in concentrated sulphuric acid with slight development of heat, yielding a greenish-brown solution; it is very readily hydrolysed by alkalis, even in the cold, yielding various compounds which are fully described below.

Dihydrazone of Ethyl Dimethyldiacetylpimelate,

$N_2HPh{:}CMe{\cdot}CMe(COOEt){\cdot}[CH_2]_3{\cdot}CMe(COOEt){\cdot}CMe{:}N_2HPh$.

Ethyl dimethyldiacetylpimelate combines readily with phenylhydrazine (2 mols.) yielding the dihydrazone, with elimination of water. The dihydrazone is easily prepared by heating the ethereal salt (5 grams) with a slight excess of the theoretical quantity of phenylhydrazine (4 grams), first at 100° for three hours, and then at 120° for 15 minutes. The product is dissolved in ether, the solution filtered from a trace of a crystalline compound (referred to below), washed repeatedly with very dilute hydrochloric acid, then with water, dried, and evaporated, when the dihydrazone remains as a reddish-yellow oil. Two samples of this oil, prepared from different samples of ethyl dimethyldiacetylpimelate, were kept over sulphuric acid under reduced pressure for 36 hours, and then analysed with the following results:—

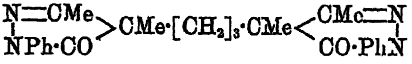
I. 0·3592 gram substance gave 32·95 c.c. of nitrogen, measured at 11° under a pressure of 745 mm.

II. 0·2956 gram substance gave 27·3 c.c. of nitrogen, measured at 13° under a pressure of 745 mm.

	Calculated for $C_{29}H_{40}N_4O_4$.	Found. I	Found. II.
N	11·0 per cent.	10·7	10·7 per cent.

This dihydrazone is a reddish-yellow, very viscous oil; it seems to undergo gradual decomposition if kept over sulphuric acid. It is insoluble in water and soda, and only very sparingly soluble in concentrated hydrochloric acid, but it dissolves freely in concentrated sulphuric acid, and is miscible with alcohol, ether, glacial acetic acid, &c., in all proportions.

The crystalline compound just referred to was obtained in both preparations of the dihydrazone, although quite different samples of the ethereal salt were employed; the quantity produced from 8 grams of the ethereal salt is only about 0·1 gram, if as much, so that we were unable to determine its composition; its formation is probably due to the presence of a trace of impurity in the ethyl dimethyldiacetylpimelate. On adding ether to its alcoholic solution, it is deposited in colourless, lustrous plates which begin to turn brown at 180°, and decompose completely at 200°; it is practically insoluble in ether and cold benzene, but moderately easily soluble in acetone and hot water, and readily in alcohol. Its aqueous solution gives no coloration with ferric chloride, and, as far as could be ascertained with the small quantity at our disposal, it does not give any reaction with nitrous acid.

It has been shown by Knorr (*Annalen*, **238**, 200) that dialkyl derivatives of ethyl acetoacetate and ethyl benzoylacetate, like the simple ethereal salts themselves, can be converted into pyrazolone derivatives; it seemed probable, therefore, that a dipyrazolone derivative, of the constitution  $\left.\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{NPh{\cdot}CO}\end{array}\right>\mathrm{CMe{\cdot}[CH_2]_3{\cdot}CMe}\left<\begin{array}{l}\mathrm{CMe{=}N}\\ \mathrm{CO{\cdot}PhN}\end{array}\right.$ would be obtained on heating the dihydrazone described above. Several attempts were made to bring about this change, but without success; when the dihydrazone is heated at 160—180°, or at even higher temperatures, it darkens in colour, but otherwise seems to be unchanged, and the evolution of alcohol cannot be observed; the residual oil resembles the dihydrazone in properties, is readily and completely soluble in ether and other organic solvents, and shows no signs of crystallising, even when cooled to 0°.

Bye-products obtained in the Preparation of Ethyl Dimethyldiacetylpimelate.

The bye-product which is obtained in preparing ethyl dimethyldiacetylpimelate is an almost colourless oil with a pleasant, fruity odour; it seems to consist of a mixture of ethyl methylallylacetoacetate and regenerated ethyl methylacetoacetate, these two compounds being probably produced in the following manner:—

$$CH_3{\cdot}CO{\cdot}CMeNa{\cdot}COOEt + CH_2Br{\cdot}CH_2{\cdot}CH_2Br = COOEt{\cdot}CAcMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br + NaBr.$$

$$COOEt{\cdot}CAcMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br + CH_3{\cdot}CO{\cdot}CMeNa{\cdot}COOEt = COOEt{\cdot}CAcMe{\cdot}CH_2{\cdot}CH{:}CH_2 + CH_3{\cdot}CO{\cdot}CHMe{\cdot}COOEt + NaBr.$$

The quantity of this bye-product, separated from the ethyl dimethyldiacetylpimelate either by distilling with steam or by fractional distillation, is about 50 per cent. of the original oil. It rapidly decolorises bromine-water, and reduces alkaline solutions of potassium permanganate in the cold, reactions which indicate the presence of an unsaturated compound, such as ethyl methylallylacetoacetate; its alcoholic solution gives with ferric chloride the same violet coloration as is produced with ethyl methylacetoacetate. All attempts to isolate the allyl derivative by fractional distillation were unsuccessful, although a liquid can be obtained which does not give a reaction with ferric chloride; it is possible, however, to obtain from the mixture a small quantity of pure ethyl methylacetoacetate, as is shown by the following analysis of a fraction collected between 185° and 187°:—

I. 0·2364 gram substance gave 0·5067 gram CO_2 and 0·1780 gram H_2O.

II. 0·2044 gram substance gave 0·4354 gram CO_2 and 0·1526 gram H_2O.

	Calculated for $C_7H_{12}O_3$.	Found.	
		I.	II.
C	58·3 per cent.	58·4	58·1 per cent.
H	8·3 "	8·4	8·3 "
O	33·4 "	33·2	33·6 "

Ethyl αα′-Dimethylpimelate, $COOEt{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOEt$.

In one of the earlier experiments on the preparation of ethyl dimethyldiacetylpimelate, it was found that on fractionating the crude product, obtained by the interaction of ethyl sodiomethylacetoacetate and trimethylene bromide, under reduced pressure (55 mm.), practically the whole passed over below 190°, a considerable quantity boiling constantly at 178—180°. As in previous experiments, about 50 per cent. of the crude product passed over at a temperature above 200°, and as, moreover, the boiling point of ethyl dimethyldiacetylpimelate had been found to be about 235° (55 mm.), it was clear that the reaction had not taken the usual course.

The experiment was, therefore, repeated under exactly the same conditions, but with the same result; practically the whole of the crude product passed over below 200° (55 mm.), a large quantity boiling constantly at about 180°, and, seemingly, not a trace of ethyl dimethyldiacetylpimelate had been produced.

In both operations the portions of the oil passing over between 175° and 182° were collected separately; each of these fractions was again distilled under the same pressure (55 mm.), and the portions boiling constantly at 178—180° collected separately. The two preparations were colourless, had a neutral reaction, and, on analysis, gave the following results:—

I. 0·1854 gram substance gave 0·4325 gram CO_2 and 0·1653 gram H_2O.

II. 0·1785 gram substance gave 0·4160 gram CO_2 and 0·1556 gram H_2O.

	Calculated for			Found.		
	$C_{17}H_{28}O_6$.	$C_{13}H_{24}O_4$.		I.	II.	
C......	62·19	63·93	per cent.	63·62	63·46	per cent.
H......	8·53	9·83	,,	9·90	9·69	,,
O......	29·28	26·24	,,	26·48	26·85	,,

It will be seen that these results agree well with those required by a compound of the composition $C_{13}H_{24}O_4$, but differ widely, especially as regards the percentage of hydrogen, from those required by ethyl dimethyldiacetylpimelate, $C_{17}H_{28}O_6$. Although the new compound boils at a considerably lower temperature than ethyl dimethyldiacetylpimelate, its boiling point is much higher than that of any simple disubstituted ethyl acetoacetate which could have been produced under the conditions employed; it seemed probable, therefore, that it had been formed from ethyl dimethyldiacetylpimelate by some secondary reaction, this view being supported by the fact that the same bye-products are obtained as when the reaction takes its usual course. On further examination, it was found that the compound in question is converted, on hydrolysis, into a crystalline acid which has the composition $C_9H_{16}O_4$; it was assumed, therefore, that the neutral substance is ethyl dimethylpimelate, and the acid *aa'*-dimethylpimelic acid, $COOH{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOH$. This assumption was subsequently proved to be correct by the fact that the acid of the composition $C_9H_{16}O_4$ is identical with the *aa'*-dimethylpimelic acid which is formed by the hydrolysis of ethyl dimethyldiacetylpimelate in the manner described below.

It was observed, in later experiments, that when ethyl sodiomethylacetoacetate is treated with trimethylene bromide in absolute alcoholic solution (Kahlbaum's 99·8 per cent. alcohol), ethyl dimethyldiacetylpimelate is formed, together with the compounds of lower boiling point referred to above, but seemingly no ethyl dimethylpimelate is produced; when, however, methylated spirit which has been simply distilled over caustic lime three or four times is employed, the product contains large quantities of ethyl dimethylpimelate and compounds of lower boiling point, but no appreciable quantity of ethyl dimethyldiacetylpimelate. It would seem, then, that the formation of ethyl dimethylpimelate is due to the partial decomposition of the ethyl dimethyldiacetylpimelate by the very small quantity of soda which is present in solution when the alcohol employed is not anhydrous; assuming this to be the case—and as far as our experiments go there is no reason to doubt it—the formation of ethyl dimethylpimelate in this way is an interesting example of the instability of the atomic complex $CH_3\cdot CO\cdot\overset{|}{\underset{|}{C}}\cdot COOEt$, the acetyl group being eliminated, whilst the $\overset{|}{\underset{|}{C}}\cdot COOEt$ group remains unchanged.

Ethyl dimethylpimelate is a colourless, mobile oil, specifically lighter than water; it has a pleasant, sweet smell, but its vapours are irritating and suffocating. It boils at 190—191° under a pressure of 80 mm.. and at 178—180° under a pressure of 55 mm.; it distils under the ordinary atmospheric pressure seemingly without decomposition, but it is not volatile with steam to any appreciable extent. It is miscible with alcohol, ether, &c., in all proportions, but is only sparingly soluble in hot, and insoluble in cold, water.

$\alpha\alpha'$-Dimethylpimelic Acid, $COOH\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot COOH$.

Dimethylpimelic acid is formed, together with dimethylacetylcaproic acid and dimethyldiacetylpentane, when ethyl dimethyldiacetylpimelate is decomposed with alkalis; it was first prepared in a crystalline condition from the ethyl salt just described. In investigating the liquid (b. p. 178—180°; 55 mm.) which was obtained in some experiments in the place of ethyl dimethyldiacetylpimelate, it was found that it is quickly decomposed by boiling alcoholic potash; on evaporating the alcohol and treating the residue with water, a clear solution was obtained, but on acidifying, a small quantity of an oily product was precipitated; the solution was extracted with ether, and the dried ethereal extract evaporated, when there remained a yellowish, strongly acid syrup. This product was kept for about 24 hours over sulphuric acid and then analysed, with the following results:—

I. 0·2694 gram substance gave 0·5668 gram CO_2 and 0·2096 gram H_2O.

II. 0·1604 gram substance gave 0·3386 gram CO_2 and 0·1236 gram H_2O.

	Calculated for $C_9H_{16}O_4$.	Found. I.	Found. II.	
C........	57·44 per cent.	57·58	57·57	per cent.
H.......	8·51 ,,	8·64	8·56	,,
O......	34·04 ,,	33·78	33·87	,,

Although the analytical results agreed well with those required by a compound of the composition $C_9H_{16}O_4$, the crude product was of a yellowish colour, and seemingly impure; as it showed no signs of crystallising even when kept at 0° for some time, it was distilled under reduced pressure (53 mm.); the thermometer rose at once to 245° and the whole passed over between 245° and 255°, most boiling constantly at 250—251°. The fraction 250—251°, which had been collected separately, showed signs of crystallising after being kept for a few hours over sulphuric acid, and, on rubbing, the whole solidified to a colourless, crystalline mass; the solid compound was spread on a porous plate to free it from traces of oil, and then analysed, with the following results:—

I. 0·1749 gram substance gave 0·3668 gram CO_2 and 0·1392 gram H_2O.

II. 0·1628 gram substance gave 0·3414 gram CO_2 and 0·1277 gram H_2O.

	Calculated for $C_9H_{16}O_4$.	Found. I.	Found. II.	
C........	57·44 per cent.	57·19	57·19	per cent.
H	8·51 ,,	8·84	8·71	,,
O........	34·04 ,,	33·97	34·10	,,

These analyses show that the compound has the composition $C_9H_{16}O_4$; its method of formation led us, for the reasons stated above, to assume that it is *αα'*-dimethylpimelic acid; this view was proved to be correct by the fact that the compound is identical with the dicarboxylic acid obtained on hydrolysing ethyl dimethyldiacetylpimelate.

αα'-Dimethylpimelic acid, which has been previously purified by crystallising it twice from a mixture of benzene and carbon bisulphide, separates from hot light petroleum in well-defined twin prisms, but the impure acid is by no means easy to obtain in well-defined crystals. It is very readily soluble in cold benzene, ether, alcohol, chloroform, acetone, warm water, and hot carbon bisulphide, but only very sparingly in hot, and almost insoluble in cold, light petroleum; it is best obtained in crystals by dissolving it in hot light petroleum, or in a mixture of benzene or carbon bisulphide and light petroleum, and allowing the solution to cool slowly, but even a trace of impurity seems to prevent crystallisation; the slightly impure acid separates as an oil from all the solvents mentioned above even when the solutions are allowed to evaporate spontaneously, and it is also precipitated as an oil on adding light petroleum to a solution in benzene cooled to 0°. Although it does not crystallise readily from solvents, the oil itself solidifies moderately quickly even when slightly impure. The pure acid melts at 80—81°, boils at 250—251° under a pressure of 53 mm., and at 260—262° under a pressure of 75 mm., seemingly without decomposition; it is not volatile with steam to any appreciable extent, and its vapours have a sweet smell, recalling that of honey. It dissolves in concentrated sulphuric acid, yielding a colourless solution; when heated with phosphoric anhydride at a moderately high temperature, it yields an oil, having a strong turpentine-like odour; this reaction will be further investigated by one of us.

The *silver* salt, $C_9H_{14}O_4Ag_2$, was prepared by precipitating a neutral solution of the ammonium salt with silver nitrate; the colourless precipitate was washed well with cold water and dried, first on porous earthenware, and then at 100°. A silver determination gave the following result:—

0·2457 gram substance gave 0·1316 gram silver.

	Calculated for $C_9H_{14}O_4Ag_2$.	Found.
Ag........	53·66 per cent.	53·56 per cent.

The *barium* salt, $C_9H_{14}O_4Ba$, was also prepared by boiling an aqueous solution of the acid with excess of barium carbonate; on evaporating the filtered solution at 100°, there remained a colourless, vitreous mass, which could not be obtained in crystals by evaporating its aqueous solution over sulphuric acid. The salt was, therefore, dissolved in a little water, and the solution mixed with methyl alcohol, when a colourless, amorphous powder was precipitated; a barium determination, made with a portion of this powder dried at 100°, gave the following result:—

0·1660 gram substance gave 0·1184 gram barium sulphate.

	Calculated for $C_9H_{14}O_4Ba$.	Found.
Ba...........	42·4 per cent.	41·9 per cent.

The *ammonium* salt is obtained in colourless crystals on adding ether to an alcoholic solution of the dry salt, and then evaporating over sulphuric acid; it is readily soluble in water and alcohol.

In moderately concentrated aqueous solutions of the ammonium salt, mercuric chloride produces a yellowish, granular precipitate seemingly insoluble in hot water; ferric chloride gives a light-brown, and copper sulphate a light bluish-green precipitate, both compounds being insoluble, or only very sparingly soluble, in hot water. The zinc, lead, and calcium salts are readily soluble in cold water, and no precipitate is produced on adding solutions of these metallic salts to a solution of the ammonium salt.

The electrical conductivity of the acid was very kindly determined for us by Dr. J. Walker, who gave the following account of his experiments. "The dissociation constant for the electrical conductivity of dimethylpimelic acid at different concentrations is $K = 0{\cdot}00390$; as might be expected, this acid is stronger than pimelic acid, which gives $K = 0{\cdot}00357$."

Hydrolysis of Ethyl Dimethyldiacetylpimelate.

Ethyl dimethyldiacetylpimelate is readily decomposed by alkalis yielding, as is usually the case with compounds of this nature, both acid and neutral products; the principal compounds obtained in this way are dimethylpimelic acid, dimethylacetylcaproic acid, and dimethyldiacetylpentane, the formation of which may be represented by the following equations:—

$$\text{(1.)}\ \mathrm{COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 4KOH =}$$
$$\mathrm{COOK{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOK + 2C_2H_3O_2K + 2C_2H_5{\cdot}OH.}$$

$$\text{(2.)}\ \mathrm{COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 4KOH =}$$
$$\mathrm{CHMeAc{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOK + C_2H_3O_2K + 2C_2H_5{\cdot}OH}$$
$$\mathrm{+ K_2CO_3.}$$

$$\text{(3.)}\ \mathrm{COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 4KOH =}$$
$$\mathrm{CHMeAc{\cdot}[CH_2]_3{\cdot}CHMeAc + 2K_2CO_3 + 2C_2H_5{\cdot}OH.}$$

The relative yield of acid and neutral products depends, to a considerable extent, on the conditions under which hydrolysis takes place; as our principal object was to prepare the diketone, various experiments were made, in order to determine in what manner the best yield of this compound could be obtained. For this purpose, the behaviour of the ethereal salt with (1) barium hydroxide, (2) a mixture of glacial acetic acid and sulphuric acid, (3) cold concentrated potash, (4) hot moderately dilute potash, was investigated, in the following manner:—

(1.) When the crude ethyl salt (10 grams) is mixed with a concentrated aqueous solution of barium hydroxide (30 grams), and the mixture heated to boiling, a colourless barium salt separates from the solution, and the oil disappears completely in the course of three to four hours; on acidifying with hydrochloric acid, slight effervescence is observed and only a trace of oil is precipitated, but on extracting the solution five times with ether and evaporating the dried extract, there remains a yellowish oil (5·5 grams), which is readily and completely soluble in alkalis. The analysis of this crude acid product gave results agreeing with those required by a mixture of dimethylpimelic acid and dimethylacetylcaproic acid. It seems, therefore, that dimethyldiacetylpentane is not formed on hydrolysing ethyl dimethyldiacetylpimelate with aqueous barium hydroxide; for this reason, the reaction was not further investigated.

(2.) As many ethereal salts of ketonic acids are decomposed by acid hydrolysing agents in such a way that the ketone decomposition predominates, it seemed probable that this would also be the case with ethyl dimethyldiacetylpimelate. The following experiment showed, however, that the diketone is not produced in any quantity under the conditions employed. The ethereal salt (10 grams) was dissolved in glacial acetic acid (20 grams), a mixture of concentrated sulphuric acid (5 grams) and water (5 grams) added, and the solution heated to boiling; evolution of carbonic anhydride quickly sets in, and continues for some hours, the solution darkening considerably in colour. On adding water and distilling with steam, a small quantity of an oil, having a strong odour of turpentine, collects in the receiver, but the principal product is a thick, dark-purple liquid, which is not volatile with steam; these two products were not examined, it being evident that the above method is not suitable for the preparation of dimethyldiacetylpentane.

(3.) The action of cold concentrated alcoholic potash on the ethereal salt was next investigated, as it was thought that in this way we might obtain dimethyldiacetylpimelic acid, in accordance with the equation

$$\begin{aligned}&\mathrm{COOEt{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOEt + 2KOH =}\\&\qquad\qquad\mathrm{COOK{\cdot}CMeAc{\cdot}[CH_2]_3{\cdot}CMeAc{\cdot}COOK + 2C_2H_5{\cdot}OH.}\end{aligned}$$

This acid would probably be decomposed on heating at a suitable temperature, with evolution of carbonic anhydride, yielding the theoretical quantity of dimethyldiacetylpentane.

The experiment was carried out as follows:—A solution of potash (60 grams) in a small quantity of dilute methyl alcohol was mixed with the ethereal salt (32 grams) in the cold, and the solution kept at the ordinary temperature for about two days. The alcohol was then evaporated over sulphuric acid, the residue dissolved in water, the solution filtered from a trace of oil and carefully acidified with dilute sulphuric acid; no precipitate having been produced, the solution was extracted 12 times with ether and the dried extract evaporated, when there remained a large quantity (24 grams) of a yellowish oil. Analyses of this crude product gave results differing very considerably from those required by dimethyldiacetylpimelic acid, so that it would seem that simple hydrolysis does not take place under the above conditions; the behaviour of the product shows, however, that it contains considerable quantities of dimethylacetylpimelic or dimethyldiacetylpimelic acid. When it is heated at 200°, carbonic anhydride is evolved, and there remains a brown oil, which is only partially soluble in sodium carbonate; the insoluble oil was found, on analysis, to consist of slightly impure dimethyldiacetylpentane; the soluble portion is a mixture of dimethylpimelic acid and dimethylacetylcaproic acid, from which the former can be isolated without much difficulty. As the yield of impure diketone is only 3 grams from 32 grams of the ethereal salt, and as, moreover, the process is rather troublesome to carry out, further experiments were made, and finally the following method was adopted for the preparation of dimethyldiacetylpentane.

(4.) Crude ethyl dimethyldiacetylpimelate (120 grams), prepared as described above (p. 572), is mixed with a little alcohol, the mixture heated to boiling in a flask provided with a reflux condenser, and a moderately dilute, hot solution of potash (80 grams) in dilute alcohol slowly dropped in; as soon as the whole of the potash has been added, the alcohol is distilled off, the residue mixed with water to dissolve the potassium salts, and the ketone extracted with ether. On evaporating the ethereal solution, previously dried over anhydrous potassium carbonate, the crude ketone remains as a yellow oil. The quantity of this crude product is, as a rule, about 32—36 grams, but unless the potash is added drop by drop, the yield is considerably diminished; in one experiment, for example, the ethereal salt (95 grams) was hydrolysed with potash (70 grams), the alkaline solution being added in small quantities at a time, instead of drop by drop; the yield of crude ketone in this case was only 14 grams. The purification of the product is described under dimethyldiacetylpentane (p. 588).

The alkaline solution from which the ketone has been extracted with ether contains the potassium salts of dimethylpimelic acid and dimethylacetylcaproic acid; on acidifying with dilute sulphuric acid, the two acids are partially precipitated as a thick, yellow oil. The solution is repeatedly extracted with ether, the extract dried over calcium chloride and evaporated; the weight of the crude acid mixture obtained in this way from 120 grams of the ethereal salt is about 50 grams when the yield of ketone is 32—36 grams; in the other experiment referred to above, 95 grams of the ethereal salt gave 45 grams of the acid mixture, the yield of ketone being only 14 grams. On distilling the crude acid mixture under reduced pressure, say 65 mm., it begins to boil at about 210°, and the thermometer rises gradually to about 260°; the highest fraction solidifies partially on keeping for some time, so that by repeating the process two or three times a considerable quantity of dimethylpimelic acid can be isolated in a crystalline condition. The lower fractions, on repeated distillation, give a liquid boiling constantly at 225—227° (65 mm.); a large number of analyses have been made with samples of the liquid obtained in this way in different preparations, but the percentage of carbon found was invariably from 1 to 2 per cent. less than that required by dimethylacetylcaproic acid, as is shown by the following examples:—

I. Fraction boiling at 225—227° (65 mm.): 0·1776 gram substance gave 0·4135 gram CO_2 and 0·1550 gram H_2O.

II. Fraction boiling at 226—228° (70 mm.): 0 2051 gram substance gave 0·4725 gram CO_2 and 0·1772 gram H_2O.

	Calculated for $C_{10}H_{18}O_3$.	Found. I.	Found. II.
C	64·5 per cent.	63·5	62·8 per cent.
H	9·7 „	9·7	9·6 „
O	25·8 „	26·8	27·6 „

These results lead to the conclusion that, in spite of the considerable difference in boiling points, dimethylacetylcaproic acid cannot be completely freed from dimethylpimelic acid by fractional distillation. Various means were tried to effect the complete separation of the two compounds, but at first without success; the barium salts of the acids are both very readily soluble in water, and most of the other metallic salts are amorphous, or readily soluble. It was also found that converting the impure dimethylacetylcaproic acid into its methyl salt and fractionating the latter is of little use; the acid regenerated from the purified methyl salt gives, as before, from 1 to 2 per cent. of carbon less than the theoretical quantity. Later on it was observed that, on boiling a neutral solution of the ammonium salt of dimethylacetylcaproic acid, ammonia is evolved, and the solution becomes strongly acid; if the boiling is continued for some time, and the solution then cooled, the acid is deposited as an oil. On treating a neutral solution of ammonium dimethylpimelate in like manner, ammonia is also evolved, but only slowly, and, on cooling, no separation of acid takes place; if, after the evolution of ammonia is at an end, the solution is warmed with soda, ammonia is again evolved. It is evident, therefore, that ammonium dimethylacetylcaproate undergoes complete decomposition on boiling its aqueous solution, whereas the salt of dimethylpimelic acid is simply converted into the ammonium hydrogen salt; this difference in behaviour affords an easy means of separating the two acids. For this purpose, the crude acid mixture, obtained by hydrolysing ethyl dimethyldiacetylpimelate, is dissolved in a slight excess of ammonia, and the solution boiled in a reflux apparatus until the evolution of ammonia ceases; after cooling, the dimethylacetylcaproic acid is extracted with ether, the residual solution then mixed with dilute sulphuric acid, and the dimethylpimelic acid extracted by repeatedly shaking with ether. The crude mixture is in this way separated into two approximately equal portions, sometimes the one, sometimes the other, acid being present in rather larger quantity.

αα′-Dimethylacetylcaproic Acid, $CHMeAc\cdot[CH_2]_3\cdot CHMe\cdot COOH$.

The crude dimethylacetylcaproic acid obtained in the manner just described seems to be tolerably pure; when distilled under a pressure of 63 mm., about 90 per cent. of the oil boils constantly at 224.° Analyses of the portion boiling at 224° gave the following results:—

I. 0·1637 gram substance gave 0·3845 gram CO_2 and 0·1440 gram H_2O.

II. 0·1916 gram substance gave 0·4507 gram CO_2 and 0·1705 gram H_2O.

	Calculated for $C_{10}H_{18}O_3$.	Found. I.	Found. II.	
C........	64·51 per cent.	64·06	64·15	per cent.
H........	9·68 „	9·77	9·88	„
O........	25·81 „	26·17	25·97	„

These analytical results are considerably better than those obtained with other preparations of the acid, and there is no doubt that the method of separation just described gives a much purer product than can be obtained by fractional distillation alone. The slightly low percentage of carbon obtained on analysis seems to be due to two causes: firstly, the acid is hygroscopic; and, secondly, it seems to undergo slight decomposition on distillation, even under greatly diminished pressure. That it is free from dimethylpimelic acid was proved by estimating the quantity of potash required to neutralise the acid; dimethylacetylcaproic acid being monobasic, and dimethylpimelic acid bibasic, and the two compounds having practically the same molecular weight, the presence of even 1 per cent. of the latter would greatly influence the result :—

0·2243 gram acid, dissolved in water, required 12·2 c.c. KOH (1 c.c. = 0·005573 gram KOH), phenolphthaleïn being used as indicator.

	Calculated for $C_{10}H_{18}O_3$.	Found.
KOH	0·06753 gram.	0·06799 gram.

Dimethylacetylcaproic acid is a colourless, odourless, moderately mobile oil; its vapours have an irritating and pungent odour recalling that of burnt fat. It boils at 215—217° under a pressure of 45 mm, and at 226—228° under a pressure of 70 mm., seemingly with slight decomposition; it does not solidify when cooled to 0°. It is only sparingly soluble in cold, but more readily in hot water, and is miscible with most ordinary solvents in all proportions. It is hygroscopic; on leaving about 0·2 gram of the acid exposed to the air for a few minutes on a watch-glass, a gain in weight of about 1½ milligrams is observed. It reduces Fehling's solution on warming, and combines readily with hydroxylamine.

The *silver* salt, $C_{10}H_{17}O_3Ag$, was prepared by dissolving the acid in a slight excess of ammonia, boiling the solution until neutral, then filtering from a trace of oily impurity, and precipitating with silver nitrate; the colourless precipitate was washed by decantation, spread on porous earthenware, and then dried for 18 hours over sulphuric acid. A silver determination gave the following result :—

0·2808 gram substance gave 0·1031 gram silver.

	Calculated for $C_{10}H_{17}O_3Ag$.	Found.
Ag........	36·79 per cent.	36·72 per cent.

Silver dimethylacetylcaproate is a colourless, amorphous compound, only sparingly soluble in boiling water, from which, on cooling, it is deposited in peculiar web-like forms; it seems to undergo slight decomposition on prolonged boiling with water, and it darkens on exposure to light.

The *ethyl* salt, $C_{12}H_{22}O_3$, was obtained by dissolving the pure acid in absolute alcohol (3—4 vols.), gradually adding concentrated sulphuric acid (1 vol.), and keeping the mixture for six hours at the ordinary temperature; on adding water to the slightly brown solution, the ethereal salt is precipitated as an oil, and can be easily isolated in the usual manner. On distilling the product under a pressure of 70 mm., the thermometer rose at once to 180°, and practically the whole boiled constantly at 182—183°; the analysis of the fraction boiling at 182—183° gave the following result :—

0 2115 gram substance gave 0·5189 gram CO_2 and 0·1962 gram H_2O.

	Calculated for $C_{12}H_{22}O_3$.	Found.
C.........	67·29 per cent.	66·91 per cent.
H........	10 28 ,,	10·30 ,,
O........	22·43 ,,	22·79 ,,

Ethyl dimethylacetylcaproate is a colourless, mobile liquid with a pleasant, sweetish smell, but its vapours are rather irritating; it boils at 182—183° (70 mm.), and under the ordinary atmospheric pressure at about 250°, seemingly without decomposition. It is insoluble, or only very sparingly soluble, in water, but miscible with alcohol, ether, &c., in all proportions.

The *methyl* salt was also prepared, but from a sample of the acid which had been purified by fractional distillation only; although the product boiled very constantly at 180—181° under a pressure of 95 mm., it did not give satisfactory results on analysis, probably owing to the presence of methyl dimethylpimolate.

The barium, calcium, and zinc salts are readily soluble in water; in moderately concentrated neutral solutions of the ammonium salt, mercuric chloride produces a colourless, granular precipitate, insoluble in water, and ferric chloride a dirty-yellow precipitate which decomposes on warming.

Dimethyloximidocaproic Acid, $OH{\cdot}N{:}CMe{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COOH$.

This compound was prepared by treating pure ethyl dimethylacetylcaproate (5 grams) with hydroxylamine hydrochloride (3 grams) and potash (4 grams) in dilute alcoholic solution; after keeping for two days at the ordinary temperature, the alcohol was distilled off, the residue dissolved in water, and the solution rendered slightly acid with dilute hydrochloric acid; the oxime, which is precipitated as an oil, was extracted with ether, and the dried ethereal solution evaporated. A nitrogen determination was made with a portion of the product which had been kept for some time over sulphuric acid under reduced pressure, with the following result:—

0·2526 gram substance gave 14·9 c.c. of nitrogen, measured at 14° under a pressure of 750 mm.

	Calculated for $C_{10}H_{19}NO_3$.	Found.
N.........	6·96 per cent.	6·84 per cent.

Dimethyloximidocaproic acid is a very thick, yellowish oil with a pleasant fruity odour. It is only sparingly soluble in hot, and almost insoluble in cold water, but soluble in sodium carbonate, soda, and dilute hydrochloric acid; it dissolves freely in alcohol, ether, benzene, &c., but is practically insoluble in light petroleum.

$\alpha\alpha'$-Dimethylpimelic Acid.

The acid which remains in solution as the ammonium hydrogen salt on boiling an ammoniacal solution of the crude acid mixture obtained by the hydrolysis of ethyl dimethyldiacetylpimelate (compare pp. 583—584) is, as has been stated above, $\alpha\alpha'$-dimethylpimelic acid. After extracting the free dimethylacetylcaproic acid, the clear aqueous solution is mixed with excess of dilute sulphuric acid, repeatedly shaken with ether, and the dried ethereal extract evaporated, when there remains a thick, yellow oil. Pure dimethylpimelic acid can be easily obtained from this crude product by fractional distillation under reduced pressure (50 mm.); the portion boiling at 245—255°, usually about 70 per cent. of the whole, gradually solidifies on keeping or when rubbed with a crystal of the pure acid, and is then spread on porous earthenware.

A sample of the acid obtained in this way was titrated with potash, phenolphthalein being used as indicator; the result showed that the product is pure and free from dimethylacetylcaproic acid.

0·1814 gram substance, dissolved in water, required 20 c.c. of KOH (1 c.c. = 0·005573 gram KOH).

	Calculated for.	Found.
KOH required..	0·1120 gram.	0·1115 gram.

An analysis of the acid gave the following result:—

0·1583 gram substance gave 0·3338 gram CO_2 and 0·1226 gram H_2O.

	Calculated for $C_9H_{16}O_4$.	Found.
C.........	57·44 per cent.	57·50 per cent.
H	8·51 ,,	8·60 ,,
O	34·04 ,,	33·90 ,,

The $\alpha\alpha'$-dimethylpimelic acid obtained from ethyl dimethyldiacetylpimelate is identical with the acid prepared from ethyl dimethylpimelate in the manner previously described (p. 576); this fact shows that the last-named compound has the constitution assigned to it above.

Dimethyldiacetylpentane, $CH_3\cdot CO\cdot CHMe\cdot[CH_2]_3\cdot CHMe\cdot CO\cdot CH_3$.

The crude ketone obtained by the hydrolysis of ethyl dimethyldiacetylpimelate as described above (p. 582) is by no means pure;

on distillation under reduced pressure, say 110 mm., about 40 per cent. of the crude product passes over below 180°, about 55 per cent. between 180° and 200°, and the remainder above 200°. The pure compound can be isolated from the fraction boiling at 180—200° without much difficulty by fractionating again two or three times under reduced pressure; this process is, however, attended with considerable loss, the yield of pure diketone being only about 40 per cent. of the crude product, that is to say, about 16 grams from 288 grams of ethyl methylacetoacetate.

The following results were obtained on analysing various samples of the pure compound taken from different preparations.

I. Fraction boiling at 191—193° (105 mm.): 0·1998 gram substance gave 0·5230 gram CO_2 and 0·1952 gram H_2O.

II. Fraction boiling at 190—192° (100 mm.): 0·1810 gram substance gave 0·4734 gram CO_2 and 0·1761 gram H_2O.

III. Fraction boiling at 202—204° (150 mm.): 0·1471 gram substance gave 0·3842 gram CO_2 and 0·1441 gram H_2O.

	Calculated for $C_{11}H_{20}O_2$.	Found.		
		I.	II.	III.
C	71·74 p. c.	71·38	71·32	71·32 p. c.
H	10·87 „	10·85	10·81	10·88 „
O..........	17·39 „	17·77	17·87	17·89 „

Dimethyldiacetylpentane is a colourless, mobile oil with a faint pleasant smell; it shows no signs of crystallising even when kept at 0° for some time. It boils at 190—192° under a pressure of 100 mm., at 202—204° under a pressure of 150 mm., and when heated in small quantities it distils under the ordinary pressure, seemingly without decomposition; it is readily volatile with steam. It is specifically lighter than water, and only very sparingly soluble in hot water, but it is miscible with most ordinary organic liquids in all proportions. It does not combine with sodium hydrogen sulphite even when kept in contact with a concentrated aqueous solution of the salt for some days.

Dimethyldiacetylpentane Dioxime.

$OH{\cdot}N{:}CMe{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CMe{:}N{\cdot}OH.$

This compound was prepared as follows:—The pure diketone (4 grams) is treated, in dilute methyl alcoholic solution, with excess of hydroxylamine hydrochloride (6 grams) and a considerable excess of potash (6 grams), the solution kept for two days at the ordinary temperature, and the alcohol then evaporated; the residue is dissolved in water, the solution acidified with dilute sulphuric acid, and the oxime, which is precipitated as an oil, extracted with ether. On evaporating the dried ethereal solution, there remains an almost colourless oil which gradually solidifies to a mass of crystals; the crystalline product is first spread on porous earthenware, then dissolved in benzene, and reprecipitated by adding light petroleum, when it is deposited in colourless, microscopic crystals.

A nitrogen determination, made with a portion of the pure dioxime, gave the following result:—

0·1164 gram substance gave 13 3 c c. of nitrogen measured at 11° under a pressure of 740 mm.

	Calculated for	Found.
N	13 08 per cent.	13·26 per cent.

Dimethyldiacetylpentane dioxime crystallises from boiling water, in which it is only sparingly soluble, in concentrically grouped needles, and from a mixture of benzene and light petroleum, in compact, microscopic crystals melting at 95—96°; it is readily soluble in cold benzene, ether, and alcohol, but insoluble, or only very sparingly soluble, in light petroleum. It dissolves freely in concentrated hydrochloric acid, but is only sparingly soluble in warm soda.

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LIII.—*The Molecular Refraction and Dispersion of Various Substances in Solution.*

By Dr. J. H. Gladstone, F.R.S.

The present paper is a continuation of that which I had the honour of laying before the Chemical Society in March last (this vol, p. 290). It deals entirely with solid and gaseous substances dissolved in various liquids.

The specific refraction of the solvent being known, and the strength and specific refraction of the solution being ascertained, it is easy to calculate what will be the specific refraction of the substance dissolved, provided the solvent does not exert any special chemical action on it.

The following table comprises several organic substances on which I have made observations. The nature of the solvent and the percentage of the dissolved substance are given, together with the calculated results. The actual indices of refraction and the sp. gr. of the solutions are not given, as they would be of no value without the corresponding observations upon the solvents used, which would needlessly add to the bulk of the table.

TABLE I.—*Organic Substances.*

Substance.	Formula.	Solvent.	P. c. of subst.	R_λ	R_D.	R_F.	R_H.
Terpene hydrate....	$C_{10}H_{22}O_3$.	alcohol	17·69	87·42	88·28	—	91·50
Terpilene dihydrochloride.........	$C_{10}H_{18}Cl_2$.	eth. alc.	21·04	92·18	93·18	—	96·45
Camphor..........	$C_{10}H_{16}O$ ..	alcohol	45·18	73·51	74·32	—	76·98
Bromocamphor	$C_{10}H_{15}BrO$.	„	10·62	87·87	87·99	—	92·88
Camphoric acid	$C_{10}H_{16}O_4$ ..	„	39·81	82·84	83·74	—	86·66
Benzyl-camphor	$C_{17}H_{22}O$ ..	toluene	6·6	122·83	125·69	128·81	132·62
„ „	„ ..	„	9·3	123·34	126·36	127·69	133·05
Benzal-camphor	$C_{17}H_{20}O$ ..	„	9·0	128·27	—	136·67	145·71
„ „	„ ..	„	19·94	130·42	134·55	139·26	—
„ „	„ ..	„	20·70	130·09	133·69	138·19	—
Menthol..........	$C_{10}H_{20}O$ ..	benzene	58·54	79·15	80·00	—	82·64
Phenyl ether.......	$C_{12}H_{10}O$ ..	alcohol	50·60	89·54	91·44	—	98·39
Dibenzyl	$C_{14}H_{14}$	benzene	34·10	102·80	105·09	107·76	112·83
Cane-sugar.........	$C_{12}H_{22}O_{11}$..	water	65·00	118·65	—	121·23	123·38
Milk-sugar.........	„ ..	„	12·00	121·41	—	123·98	126·82
Glucose No. 1......	$C_6H_{12}O_6$ ..	„	31·71	63·18	—	64·48	65·68
„ No. 2......	„ ..	„	26·44	63·24	—	64·48	65·59
Mannite	$C_6H_{14}O_6$ ..	„	12·06	66·26	67·29	—	68·84
„	„ ..	„	12·94	66·53	—	68·21	69·06
„	„ ..	„	13·83	66·46	—	67·90	68·83
„	„ ..	„	15·38	66·38	67·33	—	68·87
„	„ ..	„	15·83	65·88	66·68	67·37	68·98

The molecular refraction and dispersion of the foregoing substances are compared in Table II with the theoretical values as deduced from the refraction and dispersion of the elements given in my previous paper already referred to.

It cannot be expected that there shall be anything like the same accordance between the experimental and calculated numbers, as is usually found in pure liquids; and in weak solutions the experimental error is greatly multiplied. Any discrepancy is proportionally greater in the molecular dispersion, as the numbers are smaller.

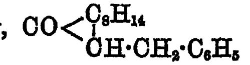
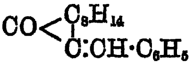
There are some points in this table (next page) which seem worthy of special remark.

Terpene Hydrate and Terpilene Dihydrochloride.—The specimens of these two bodies were kindly lent me by Professor Tilden. That the hydrate is not simply terpene combined with water is rendered certain

TABLE II.

Substance.	Formula.	Experiment.		Theory.	
		R_A.	$R_H - R_A$.	R_A	$R_H - R_A$.
Terpene hydrate	$C_{10}H_{22}O_3$	87·42	4·08	88·0	3·95
Terpilene dihydrochloride	$C_{10}H_{18}Cl_2$	92·18	4·27	93·2	4·32
Camphor	$C_{10}H_{16}O$	73·51	3·47	74·2	3·42
Bromocamphor	$C_{10}H_{15}BrO$	87·87	5·01	88·2	4·60
Camphoric acid	$C_{10}H_{16}O_4$	82·84	3·82	83·2	3·80
Benzyl-camphor	$C_{17}H_{22}O$	123·08	9·75	123·6	7·88
Benzal-camphor	$C_{17}H_{20}O$	130·25	17·44	123·2	8·60
Menthol	$C_{10}H_{20}O$	79 15	3·49	78·8	3·50
Phenyl ether	$C_{12}H_{10}O$	89·54	8·85	89·6	8·50
Dibenzyl	$C_{14}H_{14}$	102·80	10·03	101·4	9·00
Cane-sugar	$C_{12}H_{22}O_{11}$	118·65	4·73	120·6	5·26
Milk-sugar	"	121·41	5·41	"	"
Glucose No. 1	$C_6H_{12}O_6$	63·18	2·50	63·0	2·72
" No. 2	"	63·24	2·35	"	"
Mannite	$C_6H_{14}O_6$	66·30	2·62	65·0	2·72

by its optical properties. It is no longer an unsaturated compound. The theoretical calculation is made for a supposed saturated $C_{10}H_{18}O + 2H_2O$, which agrees best with the experimental figures; but other views may be taken as to the manner in which the atoms of oxygen are combined. The dihydrochloride is also a saturated substance, as might be expected.

Camphor Group.—Camphor is believed on chemical grounds to be a saturated compound; and the refraction and dispersion of itself, its bromine substitution compound, and its acid oxide prove this to be the case. Indeed, the experimental figures in the table, like those previously published, are slightly lower than the theoretical, so far as refraction is concerned. The benzyl- and benzal-camphor were kindly placed at my disposal by M. Haller, of Nancy, who said the crystals, especially of the second, were extremely refractive. In the table, the theoretical value is reckoned according to the formulæ given me by M. Haller, namely,  $\mathrm{CO}<\begin{array}{l}\mathrm{C_8H_{14}}\\ \mathrm{CH{\cdot}CH_2{\cdot}C_6H_5}\end{array}$ and  $\mathrm{CO}<\begin{array}{l}\mathrm{C_8H_{14}}\\ \mathrm{C{:}CH{\cdot}C_6H_5}\end{array}$ respectively. It will be seen that while in the first compound the molecular refraction does not exceed that of the theory, the molecular dispersion does so by a large quantity. In the second compound, which only differs from the first by the loss of H_2 and the consequent double linking, both the refraction and the dispersion are vastly greater than can be accounted for; indeed, the dispersion is just about twice the calculated amount. I am informed that both these substances in solution exhibit molecular rotation, and that the benzal compound possesses about four times as much rotatory power as the other.

Dibenzyl.—This substance exhibits optical properties rather higher than is warranted by the formula $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$, for which the theoretical values are calculated.

Sugar Group.—The optical properties are conclusive against the old supposition that these substances are carbohydrates, that is, they do not give the values warranted by the supposition that the $(H_2O)_n$ are really so many molecules of water; on the other hand, they give no support to the view that the sugars are unsaturated compounds. Taking the ordinary values for hydrogen and oxygen, and assuming that the sugars are saturated compounds, we get the figures given in the table.

TABLE III.—*Inorganic Acids.*

Acid.	Formula.	Per cent. of acid.	R_A.	R_D.	R_F.	R_G.	R_H.
Hydrochloric	HCl	5·13	14·99	—	15·52	—	16·19
”	”	8·67	14·45	—	15·41	—	15·77
”	”	10·42	14·44	—	15·30	—	15·74
”	”	11·48	14·47	—	15·10	—	15·61
”	”	14·93	14·21	14·64	—	—	15·47
”	”	16·71	14·27	—	15·05	—	15·49
”	”	20·32	14·15	—	14·89	—	15·45
”	”	25·40	14·15	—	14·83	—	15·20
”	”	28·73	14·06	—	14·74	—	15·24
”	”	31·20	14·06	—	14·73	—	15·23
”	”	31·26	13·98	14·30	14·67	—	15·16
”	”	36·09	13·92	—	14·58	—	15·07
Hydrobromic	HBr	15·47	20·66	—	22·05	—	23·20
”	”	24·60	20·45	—	21·65	—	22·40
”	”	39·71	20·13	—	21·25	21·74	22·26
”	”	56·00	19·97	—	21·06	21·55	—
”	”	65·59	19·70	—	20·77	21·24	—
Hydriodic	HI	20·77	31·87	—	34·42	—	36·06
”	”	31·77	31·56	—	33·87	34·90	35·97
”	”	61·95	30·94	—	33·27	34·46	35·55
”	”	65·10	30·75	—	32·96	—	35·15
”	”	67·02	30·62	—	32·84	—	—
Chloric	$HClO_3$ ...	20·68	21·08	—	21·87	—	22·37
”	” ...	”	20·74	—	21·38	—	21·87
Perchloric	$HClO_4$ ...	17·30	19·86	—	20·40	—	20·92
Iodic	HIO_3	62·67	33·19	—	34·93	—	36·72
Nitric	HNO_3....	43·10	16·85	—	17·60	—	18·21
”	”	69·60	16·39	—	16·99	—	17·55
”	”	98·70	16·22	—	16·76	—	17·25
Selenious	H_2SeO_3 ..	15·40	26·39	26·65	—	—	27·76
Selenic	H_2SeO_4 ..	9·36	24·60	25·76	—	—	26·11
Metaphosphoric.....	HPO_3 ...	28·91	17·83	18·00	—	—	18·56
”	” ...	35·07	17·99	18·25	—	—	18·73
”	” ...	38·83	18·73	19 00	—	—	19·53

Cane-sugar, as in specimens previously examined, shows a refraction and especially a dispersion rather smaller than might have been expected; milk-sugar and glucose* are more accordant with theory, whilst mannite, which is allied to the sugars, is a little high in refraction. If these differences are real they offer another means of investigating the rational constitution of this natural group of bodies.

In Table III are given observations on aqueous solutions of inorganic acids

In Table IV the molecular refraction and dispersion of these different acids are given as experimentally determined, and as calculated from the atomic refraction and dispersion of their constituent elements.

TABLE IV.

Acid.	Formula	Experiment.		Theory.	
		R_A	$R_H - R_A$	R_A	$R_H - R_A$.
Hydrochloric	HCl	13·92 to 14·99	1·05 to 1·32	11·2	0·49
Hydrobromic	HBr	19·70 „ 20·66	2·04 „ 2·54	16·6	1·07
Hydriodic	HI	30·62 „ 31·87	4·19 „ 4 61	25·8	2 64
Chloric	$HClO_3$	20·91	1·21	19·6	0·79
Perchloric	$HClO_4$	19·86	1·06	22·4	0·89
Iodic	HIO_3	33·19	3·53	34·2	2·94
Nitric	HNO_3	16·22 to 16·85	1·03 to 1·36	15·4	0·80
Selenious	H_2SeO_3	26·39	1·37	41·1	—
Selenic	H_2SeO_4	24·60	1·51	43·9	—
Metaphosphoric	HPO_3	17·83 to 18·73	0·73 to 0·80	28·6	3·42

It will be seen at once from the above table that the experimental numbers are greatly in excess in some instances, whilst in others the opposite is the case.

Hydracids.—It was early recognised that the molecular refraction of the hydracids in aqueous solution was decidedly higher than the sum of the refraction of hydrogen and the halogen as determined from the paraffin compounds. This observation is now extended to the dispersion, where the comparative difference is even more striking. The same fact was observed by Perkin (Trans., 1889, 55, 702, &c.) in regard to the molecular magnetic rotation of these acids dissolved in water; he also remarked that the rotation due to the acid was greater in a dilute than in a strong solution, and that, in fact, the molecular rotation increased with the dilution up to a certain point, where it remained nearly constant. The preceding table shows that a similar gradual increase occurs also in the molecular refraction of each of the hydracids; it is evident also in the molecular dispersion of hydrochloric acid, and apparently so in hydrobromic and hydriodic acids.

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* The specimens of glucose were supplied by Messrs. Hopkin and Williams as "dextrose" and "pure grape-sugar"; but it is unlikely they were chemically pure substances.

There is still another point of resemblance between the optical and the magnetic effects. Perkin observed that the divergence of the experimental from the theoretical rotation was much greater with hydrobromic than with hydrochloric acid, and far greater still with hydriodic acid. The same holds good both with the molecular refraction and molecular dispersion, though, as usual, the differences are wider in the case of the magnetic than in the case of the optical properties. The actual numbers for this divergence are not given, pending a more careful consideration of the subject. I have reason also to think that the temperature somewhat modifies the result.

Nitric Acid.—The molecular refraction of nitric acid seems to be slightly increased by its union with water, as before observed. The molecular dispersion shows a more decided increase. In both cases, the optical effect is greater in the weaker solutions.

Selenious and Selenic Acids.—The optical properties of these two acids, like those of the corresponding sulphur compounds, are vastly less than what would be expected on adding together the values of their constituents.

Metaphosphoric Acid.—The same remark applies to this acid. This particular case, and others indicating the small refraction of high oxides, were referred to in my lecture on Refraction Equivalents before this Society in 1870.

In the above table the lower value of oxygen is adopted, except in the case of nitric acid and metaphosphoric acid, in which one atom of oxygen is regarded as doubly linked. Of course other views may be taken of the constitution of these bodies; but they will not materially affect the general conclusions.

TABLE V.—*Salts and Alkalis.*

The solvent is always water, except in the case of one determination of ammonia, and the potassium ethylate, in which alcohol was employed. The tin protochloride solution contained also some hydrochloric acid. The arrangement is alphabetical, for convenience of reference.

The following table (next page) will afford data for the revision of the refraction equivalents of the different metals, and of the electronegative elements with which they are combined. In such a revision it will be necessary to consider these observations in connection with those

TABLE V.

Substance.	Formula.	P. c. of subst.	R_A.	R_D.	R_F.	R_G	R_H.
Aluminium ammonium alum	$\left.\begin{matrix}Al_2\\(NH_4)_2\end{matrix}\right\}(SO_4)_4$	4·62	110·00	—	—	—	112·06
Aluminium sodium alum	$Al_2Na_2(SO_4)_4$.	21·39	97·17	98·20	—	—	100·34
Aluminium sulphate	$Al_2(SO_4)_3$ ...	26·93	69·54	70·78	—	71·78	72·03
"	" ...	27·35	70·26	—	—	—	73·27
" "	" ...	28·03	70·17	—	—	—	73·21
Ammonia	NH_3	13·40	9·08	—	9·36	—	9·60
"	"	19·92	8·90	—	9·19	—	9·42
"	"	21·40	9·09	—	9·33	—	9·58
"	"	33·40	8·97	—	9·22	—	9·45
"	"	34·80	8·78	—	9·04	—	9·29
" (in alc.)...	"	11·30	8·80	—	—	—	9·25
Ammonium formate.	NH_4CHO_2 ..	25·54	23·21	23·59	—	—	24·59
" chlorate.	NH_4ClO_3....	4·83	30·45	—	31·71	—	33·31
" "	"	4·53	29·51	—	31·48	—	33·14
" "	"	21·75	28·75	—	29·49	—	30·01
" perchlorate	NH_4ClO_4....	6·13	30·40	—	30·90	—	30·90
Ammonium sulphate	$(NH_4)_2SO_4$...	33·91	39·86	—	—	—	41·53
" dichromate	$(NH_4)_2Cr_2O_7$.	10·32	85·81	90·65	—	—	—
Barium chloride	$BaCl_2$.......	24·17	38·94	39·97	—	—	41·78
" chlorate	$BaCl_2O_6$	22·70	54·09	—	55·35	—	56·38
" "	"	23·75	52·72	53·36	53·99	—	54·95
" formate	$Ba(CHO_2)_2$..	18·00	40·01	—	—	—	43·04
" acetate	$Ba(C_2H_3O_2)_2$.	36·90	56·16	56 99	—	—	58·86
Calcium chloride....	$CaCl_2$	41·75	32·22	—	33·35	—	34·46
" "	"	77·36	34·45	—	35·50	—	36·38
" bromide....	$CaBr_2$	41·36	43·50	44·49	—	—	47·67
" acetate	$Ca(C_2H_3O_2)_2$.	26·33	49·84	50·77	—	—	52·45
Cerium chloride	$CeCl_2$	18·84	34·34	34·98	—	—	36·58
" "	"	13·42	34 30	35·37	—	—	37·54
Chromium sulphate..	$Cr_2(SO_4)_3$ ...	31·82	82·40	—	85·41	—	—
Didymium chloride..	$DiCl_2$	3·75	38·3	38·3	—	—	39·8
" nitrate ...	$Di(NO_3)_3$ ...	9·48	45·91	46·96	—	—	49·53
" sulphate..	$DiSO_4$	5·64	32·9	34·4	—	—	35·2
Ferric chloride......	$FeCl_3$.......	27·95	50·73	52·64	—	—	—
Iridium chloride	$IrCl_4$........	7 90	74·5	79·3	—	—	—
Lanthanum chloride .	$LaCl_3$.......	2·30	37·0	37·5	—	—	39·5
" "	"	3·19	37·4	—	—	—	40·4
" nitrate..	$La(NO_3)_2$ ...	3·85	44·2	14·7	—	—	46·6
Lead acetate........	$Pb(C_2H_3O_2)_2$	24·8	61·87	66·44	—	—	70·24
Lithium nitrate.....	$LiNO_3$	35·09	17·87	18·25	—	—	19·35
" acetate	$LiC_2H_3O_2$ ...	28·70	23·35	—	—	—	24·70
Magnesium iodide ..	MgI_2	61 75	60·02	62·28	—	—	—
" acetate ..	$Mg(C_2H_3O_2)_2$	31·50	46·25	46·88	—	—	48·69
Potassium bromide..	KBr........	35·09	25·25	—	—	—	27·42
" iodide ...	KI	59·74	35·85	36·88	—	—	40·23
" chlorate..	$KClO_3$	5·37	26·16	27·48	—	—	28·37
" nitrite ...	KNO_2	16·93	18·57	—	19·37	19·48	—
" "	"	28·20	19·04	19·34	19·74	20·01	—
" "	"	36·82	18·83	—	19·60	19·92	20·06?
" "	"	38·50	18·94	—	19·63	19·98	20·01?

TABLE V—*continued.*

Substance.	Formula.	P. c. of subst.	R_A.	R_D.	R_F.	R_G.	R_H.
Potassium sulphate..	K_2SO_4	7·13	33·4	33·8	—	—	34·6
„ sulphate..	„	„	32·1	32·2	—	—	33·1
„ „	„	„	31·6	32·7	—	—	32·5
„ selenate..	K_2SeO_4	15·21	36·21	36·75	—	—	38·25
„ hydrate ..	KHO	49·50	12·60	12·82	—	—	13·35
„ cyanide ..	KCN	33·20	17·14	—	17·63	—	18·11
„ auric cyanide..............	$KAuC_2N_2$ ...	7·09	50·5	52·1	—	—	54·9
Potassium cobalticyanide..........	$K_3CoC_6N_6$...	16·12	100·11	101·94	—	—	108·22
Potassium ethyl sulphate.........	$KC_2H_5SO_4$ ..	27·28	41·59	42·02	—	—	43·00
Potassium formate..	$KCHO_2$.....	62·43	19·56	19·84	20·14	—	20·64
„ „	„	66·61	20·03	20·31	—	—	21·10
„ „	„	69·38	19·95	20·24	—	—	21·03
„ carbonate	K_2CO_3......	41·30	28·24	—	29·01	—	29·55
„ „	„	49·60	28·59	—	29·38	—	29·98
„ oxalate...	$K_2C_2O_4$......	25·00	37·77	—	38·90	—	39·93
„ „ ...	„	25·30	37·16	—	38·32	—	39·22
„ ethylate..	KC_2H_5O	26·0	28·59	—	29·44	29·74	30·41
Silver nitrate.......	$AgNO_3$	60·56	28·05	28·65	—	—	30·53
„ potassic cyanide	$AgK(CN)_2$...	18·96	41·06	41·69	—	—	44·21
Sodium chlorate	$NaClO_3$	43·48	22·04	—	22·56	—	23·09
„ bromate.....	$NaBrO_3$.....	26·08	29·32	—	30·25	—	31·16
„ iodate	$NaIO_3$......	5·76	38·27	—	41·19	—	42·46
„ nitrate......	$NaNO_3$......	45·10	18·64	18·96	19·37	19·77	20·11
„ nitrite......	$NaNO_2$......	28·32	15·24	15·55	—	—	16·67
„ „	„	43·90	15·81	—	16·42	16·75	16·91
„ sulphate	Na_2SO_4......	30·04	26·56	—	—	—	27·60
„ „	„	17·75	28·71	28·96	—	—	29·75
„ hydrate	$NaHO$	31·00	9·25	9·44	—	—	9·92
„ „	„	34·80	9·33	—	9·76	—	10·00
„ formate	$NaHCO_2$....	37·28	16·58	—	17·07	—	17·53
„ „	„	41·39	16·63	16·76	—	—	17·55
„ „	„	44·99	16·60	16·88	—	—	17·59
„ carbonate ...	Na_2CO_3	9·32	22·46	—	—	—	23·88
„ „ ...	„	10·50	22·18	—	22·90	—	23·71
„ „ ...	„	13·77	22·02	—	22·71	23·07	23·16
„ „ ...	„	16·30	21·60	22·24	22·50	22·79	23·07
Tin protochloride...	$SnCl_2$.......	35·0	48·70	50·15	—	—	55·04

previously recorded by me and with those of Kanonnikoff and Van der Willigen. It will afford means also for determining the dispersion equivalents, with the help of the other observations previously published.

A few points may be noted with advantage at the present time.

Ammonia.—The series of determinations given above indicate 8·9 as the molecular refraction, and 0·50 as the molecular dispersion of NH_3. These would appear to be the same whatever the strength of the solution; and to be very nearly the same when dissolved in alcohol. They agree with what would be arrived at by adding together the previously received values for hydrogen and nitrogen, viz., 1·3 and 5·1 for R_A, and 0·04 and 0·38 for $R_H - R_A$, respectively; which will give 9·0 for the refraction, and 0·50 for the dispersion. This uniformity is in strong contrast with the behaviour of the hydracids when combined with water.

Cerium, Didymium, and Lanthanum.—The observations given above are sufficient to afford us determinations of the values of this group of metals. Taking the value of potassium at 7·85, which is the latest result arrived at after a very full investigation, the value of chlorine in dissolved salts amounts to 10·95, of NO_3 to 14·25, and of SO_4 to 17·5.

This will give for the value of the three metals:—

Metal.	Atomic weight.	From the chloride.	From the nitrate.	From the sulphate.
Cerium	92·0	12·42	—	—
Didymium............	96·0	16·4	17·4	15·4
Lanthanum	90·2	15·3	15·7	—

Both the didymium and lanthanum are subject to considerable error on account of the weakness of the solutions due to the sparing solubility of their salts. The didymium compounds also must have consisted of neodymium and praseodymium in unknown proportions.

Chlorates, Bromates, and Iodates.—In Tables III and V, these compounds are sufficiently represented to give some idea of their optical characters. At first sight it would appear that the addition of O_3 to the haloïd salt causes an inadequate increase of the molecular refraction, and a slight actual decrease in the molecular dispersion. Thus, on comparing the sodium chlorate with the known values of the chloride, we get the following numbers:—

	R_A.	$R_H - R_A$.
$NaClO_3$	22·04	1·05
NaCl...........	15·40	1·17
Difference	6·64	−0·12

The lower value for oxygen being 2·8, that of O_3 should be 8·4; and in the same way the dispersion should be about 0·3. Similar figures to those obtained from the sodium salt for the additional O_3

are given by the chlorates of potassium, ammonium, and barium, and by chloric acid, and by the bromate and iodate of sodium. This might very naturally be regarded as analogous to the decreased refraction of the higher oxides of sulphur, phosphorus, arsenic, &c., already noted; but I believe the reason is a totally different one. The haloïd salts in solution, as has been explained before, have a refraction higher than what would be expected from the ordinary value of the halogen and the metal. In the case of chlorides, this amounts to about 1·0; in the case of bromides and iodides somewhat more. If we suppose this unexplained increase not to take place in the case of chlorates, bromates, and iodates (any more than it does in nitrates), it will fairly account for the experimental results. The value of ClO_3 for the line A would thus be about 17·6, calculated from the sodium compound, 18·5 from the ammonium compound, 18·3 from the potassium compound, and 18·8 from the barium compound, giving a mean of 18·3. The value of BrO_3 from the sodium compound would be 24·9, while that of IO_3 from the sodium compound would be 33·8. These are by no means improbable figures, judging from the value of the halogens in the paraffin compounds, and seem to indicate that the salts of the three oxidated halogens, when dissolved in water, are normal in respect to their optical properties.

LIV.—*Volatile Platinum Compounds.*

By W. PULLINGER, Brackenbury Scholar of Balliol College, Oxford.

THE object of this work was to determine, if possible, the vapour density of some compound of platinum. In order to obtain a suitable substance for this purpose, and to find the best conditions under which the trials could be made, some miscellaneous phenomena were observed, worthy of note, but apparently unconnected with the subject.

The only volatile compounds of platinum hitherto known are those described by Schützenberger (*Ann. Chim. Phys.* [4], 21, 350; *Annalen*, Suppl. 8, 242) in the year 1872. They were obtained by passing alternately streams of chlorine and carbon monoxide over platinum sponge heated at 250° in a combustion tube by means of a gas-furnace. The volatilised substance was collected in a suitable receiver. In this manner, Schützenberger obtained a mixture of three volatile compounds, namely, carbonyl chloroplatinite, $CO,PtCl_2$, dicarbonyl chloroplatinite, $C_2O_2,PtCl_2$, and sesquicarbonyl chloroplatinite, C_3O_3,Pt_2Cl_4.

Now if we follow out the instructions given by Schützenberger, substituting a small furnace for the oil-bath in which he heated the tube, we obtain another yellow substance, which remains behind after the volatile compounds have been driven from the heated part of the tube. This compound occupies the same position as the platinum originally did, nor can any amount of heating volatilise it. When hot, it is brick-red, and, on cooling, changes to a bright canary-yellow. It was obtained in two different experiments, but was only homogeneous in the first. From the method of formation, it seemed probable that the product was a combination of platinum, chlorine, and carbon monoxide, since it was not formed till the latter gas had been passed over the platinum chloride for a considerable time. It absorbed water from the air very slowly. An analysis of the substance was made in the following manner.

The *water* absorbed from the air was determined by heating the substance in an air-bath to successively rising temperatures till its weight was constant. It proved to be anhydrous at 105°.

The *platinum and chlorine* were determined by reducing the compound by pure magnesium and acetic acid.

The reduced platinum was collected and weighed. The chlorine was precipitated by silver nitrate in large excess of nitric acid, and the precipitate treated and weighed in the usual manner.

The carbon monoxide was found by difference. The percentage composition thus obtained was:—

Platinum	40·36
Chlorine	44·71
Water	4·19
Carbon monoxide	10·74

Now the water present bears no molecular ratio to the other constituents. Calculating, therefore, the percentage composition of the anhydrous substance, we obtain the values:—

Platinum	42·12	against the theoretical	42·01
Chlorine	46·66		45·89
Carbon monoxide	11·32		12·08
	100·00		100·00

which are the values calculated for a compound having the formula $PtCl_2,2COCl_2$ or $PtCl_6,C_2O_2$. The compound would, therefore, appear to be a combination of platinum dichloride with phosgene.

It was thought possible that this substance had resulted from the action of a small amount of phosgene on the platinum dichloride. An attempt was, therefore, made to obtain it by passing a stream of phosgene over the heated chloride, but without success.

Properties of the New Compound.

It is a yellow, crystalline solid, stable in air, but slightly deliquescent. It dissolves easily in water without blackening, and, on evaporation, separates from its solution in yellow crystals apparently unaltered. In alcohol it is only slightly soluble, and carbon tetrachloride dissolves scarcely any. When strongly heated, it is decomposed with evolution of chlorine and phosgene. Thus it has none of the properties characteristic of Schützenberger's compounds. It may perhaps be called phosgeneplatinum dichloride.

Specimens of carbonyl chloroplatinite, $CO,PtCl_2$, and dicarbonyl chloroplatinite, C_2O_2,Pt_2Cl_4, were next prepared in the pure state. The former was obtained by bubbling carbon monoxide for over an hour through the melted crude product; the latter, by a similar method, substituting carbon dioxide for the monoxide.

Schützenberger says that the action of water on these compounds is very complex (*loc. cit.*). This perhaps results from a secondary action which takes place between the hydrogen chloride and the undecomposed substance.

The equations given for the action of water are:—

$$(1.)\ CO,PtCl_2 + OH_2 = CO_2 + Pt + 2HCl,$$
$$(2.)\ C_2O_2,PtCl_2 + OH_2 = CO_2 + CO + Pt + 2HCl;$$

but, as Schützenberger points out, these represent only the chief actions. Now, in neither of these reactions is platinum formed as a first result of the action. If a drop of water is added to a crystal of the substance, it immediately becomes black. But both strong hydrochloric and strong nitric acid dissolve the black substance; therefore, it cannot be either platinum or platinum dichloride, for the former is soluble in neither acid, and the latter is insoluble in nitric acid. Hence, if hydrogen chloride be formed by the action of water, it will tend to keep part of the substance in solution. Schützenberger found that a very considerable quantity of platinum remained in solution; but, in presence of a large excess of water, platinum is eventually precipitated.

The Action of Various Gases.

In order to find a suitable atmosphere into which to volatilise the substances for the vapour-density experiments, the action of various gases was tried. The results are briefly as follows:—

Action of Dry Air on $PtCl_2,2CO$.—The substance is unchanged till its melting point is reached, when carbon monoxide is evolved; the residue then solidifies, melting again at 190° A little above this temperature, it decomposes with a slight sublimation.

Dry hydrogen has no action in the cold. At the melting point, the compound is at once reduced to metal with partial sublimation. If the hydrogen be burned, the flame becomes luminous, and deposits a film of platinum on the surface of porcelain introduced into the flame.

Dry chlorine has no action till from 80° to 90°, at which temperature the compound fuzes, losing carbon monoxide with effervescence. At 115° it solidifies. At 140° it fuzes again. and is decomposed.

Dry Carbon Dioxide.—Schützenberger says the substances can be distilled in this gas; but it is very difficult to volatilise them completely. A large residue of platinum dichloride is invariably left.

Phosgene had a peculiar action in the cold. Yellow drops of liquid were formed where the substance was in contact with the glass. This liquid could not be obtained in sufficient quantity for examination. A considerable quantity of the substance volatilised when the tube was heated, but complete vaporisation seemed impossible. It is also noteworthy that the compounds heated at 100° with liquid carbonyl chloride in a sealed tube are dissolved by it, and deposited again on cooling in large crystals. In a vacuum, the substance was also incompletely volatile. The only gas in which it seemed possible to determine the vapour density was carbon monoxide.

Vapour-Density Experiments.

These were at first conducted in a Victor Meyer's tube, in an atmosphere of carbon monoxide. The bottom of the bulb was lined with asbestos. A small block of the compact substance (experiments were made with both substances) was dropped directly from the stopper on to the asbestos.

Experiments were made at various temperatures varying between 200° and 400°. There was, however, no agreement between any of the results. In some cases decomposition was evident, in others the substance was not completely volatilised. Some experiments were made without asbestos, but in no single case, even at a very high temperature, and after the lapse of a considerable time, was volatilisation complete. A final attempt was made with a modified form of apparatus devised by Professor Lothar Meyer. The bulb of the apparatus is constricted in the middle. A small piece of platinum gauze rests on the constricted part. The substance is dropped directly on to the gauze. The vapour formed falls at once into the lower part of the tube, leaving the atmosphere surrounding the solid unsaturated. In this manner the whole of the substance was volatilised; but, on examining the tube, it was found that even at a temperature of 250° the vapour of the substance in the bottom part of the tube was decomposed in contact with the glass. The colour of the vapour is a dull red. It seemed evident that the vapour density of the compounds could not be determined when glass vessels were used.

Possibly the form of apparatus described above may be useful in determining the vapour densities of other solids with heavy vapours.

It was supposed possible that the corresponding bromine derivatives might be more volatile An attempt was therefore made to obtain them.

Preparation of Platinum Dibromide.

Schützenberger obtained platinum dichloride by passing chlorine over heated platinum sponge. An attempt to obtain the dibromide in the same way failed. V. Meyer and Züblin obtained the tetrabromide by heating platinum sponge with bromine and hydrobromic acid in a sealed tube at 180°, evaporating to dryness, and heating to 180° (*Ber.*, 1880, **16**, 404). It is not necessary, however, to make use of sealed tubes. If platinum sponge be simply boiled for a short time with an excess of bromine and hydrobromic acid, in a flask connected with a reflux condenser, the whole is dissolved. If the solution is then evaporated to dryness and the residue heated, bromine and hydrogen bromide are evolved. According to Topsoë, this takes place slowly at 100°, but more quickly at 200°, leaving a bright brown powder which, when washed to free it from undecomposed tetrabromide, gives a brownish-green residue of the dibromide. It is, however, very doubtful whether any dibromide is formed at the lower temperature. The residue, obtained as above, was heated in an air-bath. Some dibromide was formed at 180°. This, when thoroughly washed from the tetrabromide, had not a brownish-green colour, but was coal-black. After heating another portion at 255° for five hours, some undecomposed tertrabromide still remained, but this time the colour of the dibromide was a dark, clear brown. It would seem therefore that the colour of the product is conditioned by the temperature of its formation. A third portion was heated at 310° for four hours in a current of air. Even at this temperature a residue of tetrabromide was left. The most convenient temperature for the preparation of the dibromide was found to be about 280°.

It may be here mentioned that spongy platinum is also dissolved by a hot solution of iodine in hydriodic acid, yielding a dark-red liquid. From this, the tetraiodide can be easily obtained by evaporating it to dryness, heating the residue to 180° in an air-bath, and washing away the soluble part. The iodide thus obtained is a compound of singular stability, seeing that it can be heated with sodium carbonate to the fusing point of that salt without losing all its iodine. A rough determination of the platinum in the iodide was made by reduction with magnesium and acetic acid; this gave a percentage of 28·2 of platinum, against the theoretical 27·7.

Action of Carbon Monoxide on Platinum Dibromide.

The dibromide was contained in a small boat which was placed in a combustion tube. The end of the tube was bent into a U-shape, so as to serve as a receiver for the volatile compound. The straight part of the tube was placed in a combustion furnace, which was gradually heated; in the meantime, a slow current of dry carbon monoxide was passed over the dibromide. At the cool end of the tube a sublimate was formed, consisting of yellow and white crystals, and a brick-red powder. At about 180°, the contents of the boat melted, giving a dark-red liquid which was volatilised with difficulty; so great was the difficulty of completely volatilising this liquid, that it seemed impracticable to determine its vapour density. The sublimed substance was now melted by immersing the U-tube in a heated paraffin-bath. A current of carbon monoxide was passed over the melted substance for more than an hour, in order that a maximum amount might be absorbed. From the analogy to the chlorine compounds, it was supposed that a compound $PtBr_2,2CO$ would be formed. Such, however, was not the case. On cooling, the substance solidified to a mass of bright-red needles. The platinum and bromine in this compound were estimated by heating a weighed quantity in a platinum crucible with a very large excess of carbonate of soda. That none of the substance was volatilised was evident from examination of the crucible after ignition. The resulting platinum was washed and weighed, and the bromine in the washings was estimated in the usual way. In this and in many other analyses, the carbonate of soda was tinged a darkish-blue. This may have been due to the formation of a subbromide of sodium, corresponding to the subchloride of potassium described by Bunsen (*Ann. Phys. Chem.*, 1861, **113**, 445).

The following results were obtained.—

		I.	II.		
Percentage of	platinum,	50·44	50·33;	mean,	50·38
„	bromine,	41·504	1·03;	„	41·26
„	CO,	8·06	8·67;	„	8·36

This approximates closely enough to the constitution of a compound having the formula $PtBr_2,CO$, which has the following percentage composition:—Platinum, 50·90; bromine, 41·79; CO, 7·31. It would appear, therefore, that this compound, which may be called "carbonylbromoplatinite," does not absorb carbon monoxide at its melting point.

Properties of Carbonylbromoplatinite.

The melting points of two different specimens were taken with a delicate thermometer with the following results: (1) 177·5°, (2) 177·5°, (3) 178°, (4) 178°. Mean result 177·7°. It is bright-red and crystallises in well-defined needles. It is much less sensitive to the action of moisture than the corresponding chlorine compound. Indeed, it may be exposed to the air for a considerable time without darkening in colour. When treated with water, it first dissolves, giving a red solution, which, however, almost instantly blackens. The black product is soluble in hydrobromic acid. Absolute alcohol dissolves the substance without blackening, giving a dark-brown solution. When melted in a stream of carbon dioxide, it loses carbon monoxide, and appears to be converted into the dibromide of platinum.

In conclusion, I must express my very sincere thanks to Professor Lothar Meyer for the great assistance which he has given me. It was he who suggested the work, and he who, during its progress, aided me with very many suggestions and much personal help.

Tubingen.

LV.—*Note on a Volatile Compound of Iron with Carbonic Oxide.*

By Ludwig Mond, F.R.S., and Friedrich Quincke, Ph.D.

In a paper on the action of carbonic oxide on nickel communicated to the Society (Trans., 1890, 57, 749) by us in conjunction with Dr. Carl Langer, and which dealt with the preparation and properties of nickel-carbon-oxide, it was stated (p. 752) that all experiments to obtain a similar compound with other metals had been unsuccessful. Considering it very improbable that nickel should be the only metal forming such a compound, we have continued these experiments, more particularly with iron, under very varied conditions, and have succeeded in volatilising notable, although very small, quantities of iron in a current of carbonic oxide.

If very finely-divided iron, obtained by reducing iron oxalate in a current of hydrogen at the lowest possible temperature, exceeding but little 400°, is allowed to cool in hydrogen gas to 80°, and then treated with carbonic oxide, the issuing gas imparts a yellow colour to the flame of a Bunsen burner into which it is introduced, which continues even at ordinary temperature for several hours; and by passing it through a heated glass tube, a metallic mirror is formed at between 200° and 350°, whilst at higher temperatures, black flakes are produced.

On dissolving these mirrors, the solutions gave all the known reactions of iron in remarkably brilliant colours. The oxide obtained by dissolving the mirror in nitric acid, precipitating with ammonia, and heating to constant weight, was reduced by hydrogen. We obtained from 0·3119 gram of oxide 0·2199 gram Fe = 70·48 per cent., and from 0·4342 gram of oxide 0·3037 gram Fe = 69·94 per cent. Fe = 56, O = 16 require 70·00 per cent. There can thus be no doubt that these mirrors consist of iron. The black flakes obtained at higher temperature consist of iron and carbon. By the combustion of the substance and absorption by caustic potash of the carbonic acid formed, we found 79·30 per cent. of carbon.

However, even under the most favourable circumstances, the quantity of iron obtained in this way is very small. Treating 12 grams of finely-divided iron with carbonic oxide during six weeks, we volatilised only about 2 grams of iron. As the action of the carbonic oxide became less energetic after a time, we had to interrupt the operation and heat the iron at 400° in a current of hydrogen for about 20 minutes every five or six hours. By passing $2\frac{1}{2}$ litres of carbonic oxide per hour over the iron, the issuing gas contained at its best not more than 0·01 gram of iron, which corresponds (if we assume the volatile iron compound to have the same composition as nickel-carbon-oxide) to less than 2 c.c. of the compound in a litre of gas.

This great dilution makes the study of the properties and composition of the compound very difficult.

In passing the gas containing it through sulphuric acid, the compound is completely absorbed, but the solution decomposes very rapidly.

In passing the gases through benzene or heavy mineral or tar oils, the compound is partially absorbed, but all the substances we have tried only take up a small quantity of it. The solutions obtained are of a tawny colour, and decompose on exposure to the air, with separation of iron hydroxide.

The solutions in mineral oils boiling between 250° and 300° seemed to us the most suitable for studying the composition of the compound; but we found it impossible to exhaust it from these solutions by means of the vacuum pump.

On raising the temperature of the solution to 100° the solution remained clear, and under a pressure of 500 mm. mercury, we obtained only a small quantity of a mixture of air and carbonic oxide (from 30 c.c. of oil about 5 c.c. of gas).

On raising the temperature to about 180°, the solution turned black, from separated metallic iron, which was found to be free from carbon, and carbonic oxide was slowly evolved; this sometimes contained a very small quantity of carbonic acid, but was always quite free from hydrogen.

We have determined the quantity of iron and carbonic oxide obtained, by heating about 30 c.c. of heavy mineral oil, through which the gas containing our compound had been passed from 8 to 16 hours, in a glass vessel very nearly filled with the oil, and connected by a capillary tube to a Hempel burette filled with mercury.

The tube was heated to 100° under a vacuum of 500 mm. mercury until the volume in the burette remained constant; the tube was cooled down to measure the exact volume of this gas, and was then heated up to 180° until no more gas was evolved, which took from 1 to 2½ hours. The increase in the volume of the gas by the latter operation gave us the carbonic oxide in the compound.

The iron contained in the oil was, after dilution with other if necessary, collected on a filter and converted into oxide. The filtrate was distilled off, and the small residuum treated with hydrochloric acid and precipitated with ammonia, and the resulting small quantity of oxide of iron added to the first. In this way we obtained the following results:—

No.	Solvent.	Found.		Corresponding to		Calculated.		
		Increase of volume at 0° and 760 mm.	Fe_2O_3.	CO.	Fe.	1 atom Fe to 4 atoms CO.	Proportion of atoms CO to 1 Fe.	Quantity absorbed of $Fe(CO)_4$ = ¼CO.
		c.c.	gram.	gram.	gram.	gram.		
1...	Paraffin oil ..	31·32	0·0270	0·03917	0·01890	0·01958	4·144	7·83
2...	Petroleum oil	34·29	0·0304	0·04288	0·02128	0·02144	4·030	8·57
3...	,,	20·2	0·0174	0·02527	0·01218	0·01263	4·150	5·05
4...	Kerosine	38·18	0·0320	0·04775	0·02240	0·02387	4·264	9·54
5 ..	,, ...	50·45	0·0446	0·06310	0·03122	0·03155	4·042	12·61

These figures, although only approximate on account of the very small quantities of substance and the imperfect method we had to use for their determination, make it very probable that the volatile iron compound is iron-tetra-carbonyl, $Fe(CO)_4$, analogous to nickel-tetra-carbonyl, $Ni(CO)_4$.

LVI.—*The Lactone of Triacetic Acid.*

By J. Norman Collie, Ph.D., F.R.S.E., University College, London.

In a paper which I communicated to this Society some short time ago (this vol., p. 5, 189) on the constitution of dehydracetic acid, I pointed out that if the formula which I proposed for dehydracetic acid were the correct one, it would then be the *δ-lactone of tetracetic acid.* The following list was then given, which was intended to show the connection between the condensed acids formed from acetic acid:—

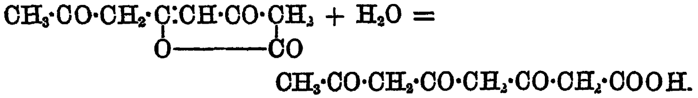
$CH_3·CO·CH_2·CO·CH_2·CO·CH_2·COOH$, Tetracetic acid.	$CH_3·CO·CH_2·COOH$, Diacetic acid.
$CH_3·CO·CH_2·CO·CH_2·COOH$, Triacetic acid.	$CH_3·COOH$. Acetic acid.

Although no acid corresponding to the triacetic acid or its lactone was then known, still, by analogy, one could predict the possibility of its existence. Since the paper on dehydracetic acid was published, I have been trying in various ways to substantiate by means of experiment the correctness of my views with regard to dehydracetic acid, and although the work on dehydracetic acid itself, is not yet finished, yet I have been able to obtain a new acid from it which seems, without doubt, to be the missing lactone of triacetic acid.

When dehydracetic acid is dissolved in strong sulphuric acid, no reaction takes place, but if the temperature is raised to about 150°, the dehydracetic acid is completely decomposed and a very large portion is converted into acetic acid.

If, however, dehydracetic acid is mixed with sulphuric acid containing about 8—10 per cent. of water, and the mixture kept at 130—135° for a few minutes and then cooled, on pouring it into water a new acid separates in crystals, which, when pure, have a much higher melting point (188—189°) than dehydracetic acid.

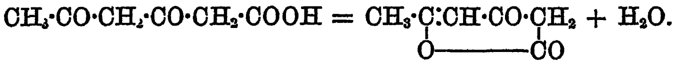
This new acid is probably the lactone of triacetic acid and is formed according to the following reactions:—

(1.) 

$$\begin{array}{l} CH_3\cdot CO\cdot CH_2\cdot C{:}CH\cdot CO\cdot CH_3 + H_2O = \\ \qquad\qquad\quad O\text{———}CO \\ \qquad\qquad\qquad\qquad CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot COOH. \end{array}$$

(2.) $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot COOH + H_2O =$

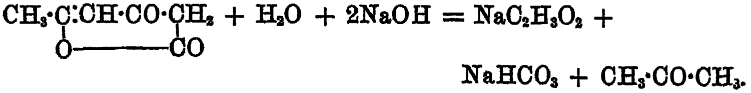
$$CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot COOH + CH_3\cdot COOH.$$

(3.) 

$$\begin{array}{l} CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot COOH = CH_3\cdot C{:}CH\cdot CO\cdot CH_2 + H_2O. \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad O\text{———}CO \end{array}$$

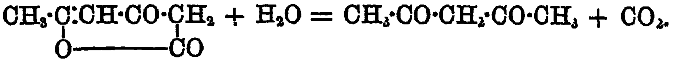
The properties of this new substance are very similar to those of dehydracetic acid. It has an acid reaction with litmus paper, yet it does not seem to form a stable ammonium salt, for its solution in ammonia, when evaporated in a vacuum, leaves a certain amount of free acid uncombined. This ammonium salt is, however, more stable than the corresponding compound of dehydracetic acid.

When warmed with alkalis, complete decomposition occurs, acetic acid, acetone, and carbonic acid being formed:—



$$\begin{array}{l} CH_3\cdot C{:}CH\cdot CO\cdot CH_2 + H_2O + 2NaOH = NaC_2H_3O_2 + \\ \quad O\text{———}CO \\ \qquad\qquad\qquad\qquad\qquad\qquad NaHCO_3 + CH_3\cdot CO\cdot CH_3. \end{array}$$

Boiled with water or with acids, it splits into acetylacetone and carbon dioxide:—



$$\begin{array}{l} CH_3\cdot C{:}CH\cdot CO\cdot CH_2 + H_2O = CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3 + CO_2. \\ \quad O\text{———}CO \end{array}$$

Treated with hydroxylamine, an oxime results, which proves the presence of a carbonyl group.

With bromine, a mono-substituted compound is obtained:—

$$C_6H_6O_3 + Br_2 = C_6H_5O_3Br + HBr.$$

The lactone cannot be distilled, but suffers decomposition when heated to a little above 200°.

From the above reactions, it seems probable that this substance is the lactone of triacetic acid. The formation of acetylacetone when boiled with acids resembles, in a striking way, the decomposition of diacetic and tetracetic acids when similarly treated:—

$$\underset{\text{Tetracetic acid.}}{CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot COOH} =$$

$$\underset{\text{Diacetylacetone.}}{CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot CH_3} + CO_2.$$

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3 + CO_2.$$

Triacetic acid. Acetylacetone.

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOH = CH_3{\cdot}CO{\cdot}CH_3 + CO_2.$$

Diacetic acid. Acetone.

In the case of dehydracetic acid, however, the diacetylacetone suffers a further loss of water, and dimethylpyrone is formed.

Lastly, when triacetic lactone is treated with ammonia, and the ammonium salt heated on the water-bath, nearly the whole is converted into a new compound, which contains nitrogen, but which does not give ammonia when boiled with strong caustic soda:—

$$C_6H_6O_3 + NH_3 = C_6H_7NO_2 + H_2O.$$

EXPERIMENTAL PART.

Action of 90 per cent. Sulphuric Acid on Dehydracetic Acid.

50 grams of dehydracetic acid were dissolved in 150 grams of dilute 90 per cent. sulphuric acid. The mixture was then heated in a flask which was immersed in an oil-bath. When the contents of the flask were at a temperature of 130°, a drop was allowed to fall into water; as soon as no crystals formed in the water after the addition of the drop of the mixture, the flask was rapidly cooled, and the contents poured into about 200 c.c. of cold water. The new compound crystallised out at once It was then recrystallised from hot water; this operation must be done as quickly as possible, for prolonged boiling decomposes the lactone to a considerable extent. By this process a yield of between 80—90 per cent. was obtained.

The new acid is more soluble in water than dehydracetic acid; it is also easily soluble in alcohol or hot acetone. In ether, benzene, chloroform, or light petroleum, it is only sparingly soluble. When pure, it crystallises in long, white needles which melt at 188—189° (corr.). An analysis gave the following numbers:—

I. 0·3870 gram substance gave 0·8130 gram CO_2 and 0·1730 gram H_2O.

II. 0·3785 gram substance gave 0·7950 gram CO_2 and 0·1650 gram H_2O.

	Calculated for $C_6H_6O_3$.	Found. I.	Found. II.
C	57·14	57·29	57·28
H	4·76	4·96	4·84

The percentage of carbon and hydrogen is, of course, the same as that required by dehydracetic acid ($C_8H_8O_4$), and also with other acids of the $C_{2n}H_{2n}O_n$ series. It was, therefore, necessary to determine the molecular weight. This was done by the Raoult method, and also by the analysis of some of the salts:—

0 5040 gram substance lowered the melting point of 39·55 grams of acetic acid, 0·38°. Molecular weight = 130.

	Calculated for $C_6H_6O_3$.	Found.
Mol. weight	126	130

The new acid has, therefore, been produced by the elimination of acetic acid from tetracetic acid:—

$$C_8H_8O_4 + H_2O = C_6H_6O_3 + C_2H_4O_2.$$

In order to verify whether acetic acid had been formed during the reaction, the mother liquors from an experiment where 20 grams of dehydracetic acid had been used were neutralised with caustic soda, and then evaporated to dryness. The residue was extracted with alcohol, and the sodium acetate thus obtained corresponded to 9 grams of acetic acid, the theoretical amount, according to the above equation being 7 grams. The sodium acetate seemed to be nearly pure, and was characterised by its properties and reactions.

The new acid reddens litmus paper, and produces an effervescence when added to potassium or barium carbonates. It seems to be monobasic, for 9·415 grams acid took 2 95 grams caustic soda for neutralisation. From the following equation:—

$$C_6H_6O_3 + NaOH = C_6H_7O_4Na,$$

the amount required is 2·98 grams.

The acid when neutralised with ammonia and evaporated in a vacuum over sulphuric acid loses some of its ammonia; it therefore in this respect resembles dehydracetic acid, and is probably not a true acid but a lactone. Most of its salts are soluble in water; even the silver salt can only be precipitated from strong solutions.

Silver Salt.—On adding a concentrated solution of either the ammonium or barium salt of the acid to a strong solution of silver nitrate, a granular, white precipitate forms.

I. 0·4120 gram salt gave 0·1895 gram Ag = 46·00 per cent. Ag.
II. 0·2235 gram salt gave 0·1035 gram Ag = 46·28 per cent. Ag.
III. 0·3170 gram salt gave 0·1460 gram Ag = 46 05 per cent. Ag.
IV. 0·4065 gram salt gave 0·4630 gram CO_2, 0·0840 gram H_2O, and 0·1880 gram Ag.

	Calculated for $C_6H_5O_3Ag$.	Found.			
		I.	II.	III.	IV.
C	30·90	—	—	—	31·00
H	2·14	—	—	—	2·14
Ag	46·25	46·00	46·28	46·05	46·25

I, II were precipitated from silver nitrate solution by the ammonium salt.

III, IV were precipitated from silver nitrate solution by the barium salt.

Potassium Salt.—The acid was exactly neutralised by potassium carbonate. The solution was evaporated to dryness, and extracted with alcohol. The alcoholic solution on evaporation left a syrup which would only crystallise when the last traces had been evaporated. The salt was therefore again dissolved in dry alcohol, and precipitated by adding dry ether. It was then obtained as a white, crystalline precipitate. This was dried in a vacuum over sulphuric acid and analysed.

0·3450 gram salt gave 0·1850 gram K_2SO_4 = 24·03 per cent. K.

	Calculated for $C_6H_5O_3K$.	Found.
K.............	23·78	24·03

Barium Salt.—This salt was prepared both from the hydrate of barium and from the carbonate. The solution of the salt evaporated either over sulphuric acid or on the water-bath dried up to a vitreous mass. It was, however, obtained as a crystalline precipitate by adding dry ether to the alcoholic solution:—

0·3900 gram salt (dried in a vacuum) gave 0·2240 gram $BaSO_4$ = 33·77 per cent. Ba.

0·4220 gram salt (dried at 130°) gave 0·2520 gram $BaSO_4$ = 35·11 per cent. Ba.

	Calculated for		Found	
	$(C_6H_7O_4)_2Ba$.	$(C_6H_5O_3)_2Ba$.	I.	II.
Ba	32·38	35·40	33·77	35·11

Nearly all the metallic salts of the lactone seem to be very soluble, as no precipitates were obtained by using a concentrated solution of the barium salt, and adding it to copper acetate, lead acetate, or mercuric chloride. The lead salt can be obtained by boiling the lactone with lead carbonate. The action is, however, very slow. The solution of the lead salt on evaporation deposits oily drops, which eventually crystallise. The barium salt of the lactone added to a neutral solution of ferric chloride gives an orange-brown precipitate.

Action of Bromine on the δ-Lactone of Triacetic Acid.

The lactone of triacetic acid reacts with bromine in a manner similar to dehydracetic acid. When the lactone is dissolved in strong acetic acid and bromine is carefully added to the well cooled mixture, after a short time a mono-brominated derivative crystallises out. The new compound is best purified by recrystallisation from acetic acid, and can be obtained in long needles, which turn black at about 200°, and decompose a few degrees higher with evolution of gas.

0·4310 gram substance gave 0·0960 gram H_2O and 0·5535 gram CO_2.

0·3015 gram substance gave 0·2805 gram AgBr = 39·59 per cent. Br.

	Calculated for $C_6H_5BrO_3$.	Found. I.	Found. II.
C	35·46	35·02	—
H..........	2·46	2·47	—
Br	39·40	—	39·59

The compound has therefore been formed by the substitution of one hydrogen atom in the lactone by bromine:—

$$C_6H_6O_3 + Br_2 = C_6H_5BrO_3 + HBr.$$

The substance possesses acid properties, and forms well defined salts, which are much more easily obtained in the crystalline condition than the corresponding ones of the lactone.

The Barium Salt.—This crystallises easily from a concentrated solution in stellate tufts of needles, and seems from its analysis to exist either as a salt of the true bromotriacetic acid or as a salt of the lactone. Some of the salt dried in the air gave the following numbers:—

0·2755 gram salt gave 0·107 gram $BaSO_4$ = 22·89 per cent. Ba.

2·0040 gram salt lost, in a vacuum over sulphuric acid, 0·0610 gram H_2O = 3·04 per cent. H_2O.

	Calculated for $(C_6H_6BrO_4)_2Ba,H_2O$.	Found.
Ba	22·87	22·89
H_2O	3·00	3·04

Another specimen was dried in a vacuum over sulphuric acid:—

0·5655 gram salt gave 0·5200 gram CO_2 and 0·0965 gram H_2O.
0·4265 gram salt gave 0·1715 gram $BaSO_4$ = 23·64 per cent. Ba.

	Calculated for $(C_6H_6BrO_4)_2Ba$.	Found. I.	Found. II.
C	24·87	25·07	—
H	2·06	1·89	—
Ba........	23·58	—	23·64

And, lastly, some was dried at 127—130°, when it ceased to lose weight:—

0·4615 gram salt gave 0·1980 gram $BaSO_4$ = 25·22 per cent. Ba.
0·3700 gram salt gave 0·1570 gram $BaSO_4$ = 24·90 per cent. Ba.

	Calculated for $(C_6H_4BrO_3)_2Ba$.	Found. I.	Found. II.
Ba........	25·13	25·22	24·90

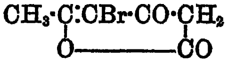
The Silver Salt.—This salt can be precipitated as a bulky mass of hair-like needles on adding a solution of the barium salt to silver nitrate. It can be recrystallised from hot water. It was dried in a vacuum and analysed:—

0·2365 gram salt gave 0·1340 gram AgBr = 32·55 per cent. Ag.

Calculated for $C_6H_4BrO_3Ag$, Ag = 34·61 per cent. Calculated for $C_6H_6BrO_4Ag$, Ag = 32·72 per cent.

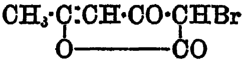
Most of the other metallic salts are extremely soluble in water, as no precipitate could be obtained on adding solutions of lead, copper, or mercury salts. With a neutral solution of ferric chloride, an orange precipitate is obtained.

When the bromine compound is boiled with water, a strong smell of bromacetone is at once produced. From this fact it seems probable that the formula is either



$$\begin{array}{l}CH_3{\cdot}C{:}CBr{\cdot}CO{\cdot}CH_2\\ \quad O\text{————}CO\end{array}$$

or



$$\begin{array}{l}CH_3{\cdot}C{:}CH{\cdot}CO{\cdot}CHBr\\ \quad O\text{————}CO\end{array}.$$

The same decomposition also occurs when a solution of the bromine compound is boiled with dilute sulphuric acid; it can, however, be boiled for some time with caustic soda without any decomposition, the brominated lactone being precipitated unchanged on the addition of an acid.

Action of Hydroxylamine on the δ-Lactone of Triacetic Acid.

The lactone was dissolved in sodium carbonate solution, and the hydrochloride of hydroxylamine then added, care being taken to have just sufficient carbonate to keep the solution alkaline. The mixture, after being left for 24 hours, was acidified, and the precipitate collected and recrystallised from hot alcohol and water; it forms long needles melting at 230—231° (corr.). Dried over sulphuric acid,

0·5255 gram substance gave 0·9755 gram CO_2.*

0·2520 gram substance gave 0 4665 gram CO_2 and 0·1385 gram H_2O.

0·3005 gram substance gave 24·8 c.c. N. at 16° and 768 mm. pressure.

	Calculated for $C_6H_9NO_3$.	Found. I.	II.	III.
C	50·35	50·62	50·48	—
H	6·29	—	6·10	—
N.........	9·79	—	—	9·73

The compound is therefore probably the oxime of triacetic acid,

$CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(NOH){\cdot}CH_2{\cdot}COOH$ or

$CH_3{\cdot}C(NOH){\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOH$.

With litmus paper it has an acid reaction.

The action of phenylhydrazine on the lactone was also tried, but although combination occurred, the resulting compound did not crystallise at all easily, so the reaction was not pursued farther.

Action of Concentrated Caustic Soda on the δ-Lactone of Triacetic Acid.

Ten grams of the lactone were boiled for a few minutes with strong caustic soda free from carbonate. The flask in which the mixture was boiled was connected with a reflux condenser. The mixture was then distilled; the distillate, on fractional separation, was found to consist of acetone and water, the acetone being recognised by its boiling point and the crystalline bisulphite compound. The residue containing the excess of caustic soda was neutralised with hydrochloric acid, when considerable effervescence of carbon dioxide occurred. The solution was then evaporated to dryness. The solid residue gave all the tests for acetic acid.

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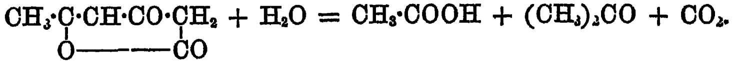
* The hydrogen determination in this combustion was spoilt, owing to oxides of nitrogen being absorbed in the sulphuric acid bulb.

The δ-lactone of triacetic acid therefore decomposes as follows:—



$$\begin{array}{l}CH_3\cdot \underset{|}{C}\cdot CH\cdot CO\cdot \underset{|}{C}H_2 + H_2O = CH_3\cdot COOH + (CH_3)_2CO + CO_2. \\ \quad\;\; O\text{————}CO\end{array}$$

Action of Heat on the δ-Lactone of Triacetic Acid.

Dehydracetic acid is capable of distillation without much decomposition; it was therefore expected that the lactone of triacetic acid would behave in a similar manner, but such was not found to be the case.

Ten grams were heated in an oil bath to about 250°; complete decomposition occurred, and 3 grams of a liquid distillate was obtained, a large quantitity of carbon dioxide was also evolved, and a considerable residue of charred matter remained in the flask. Nothing could be extracted from the charred residue except a small quantity of crystals, which were not further examined.

The distillate proved to be nearly pure acetylacetone (b. p. 137—143°).

0·1520 gram substance gave 0·3350 gram CO_2 and 0·1105 gram H_2O.

	Calculated for $C_5H_8O_2$.	Found.
C	60·00	60·10
H	8·00	8·07

Some of the characteristic copper salt was also prepared and analysed:—

0·2200 gram salt gave 0·0670 gram CuO = 24·28 per cent. Cu.
0·3048 gram salt gave 0·0920 gram CuO = 24·06 per cent. Cu.

	Calculated for $(C_5H_7O_2)_2Cu$.	Found.	
		I.	II.
Cu	24·13	24·28	24·06

Action of Pentachloride of Phosphorus on the δ-Lactone of Triacetic Acid.

This reaction was looked upon with some interest, because the chloride which ought to be formed should on reduction yield normal hexylic acid. The result of the action of pentachloride of phosphorus was, however, very disappointing. The experiment was made in several different ways, but always with the same result.

At ordinary temperatures no action took place, but, on warming, a vigorous reaction at once set in, with the invariable result that a dark-coloured mass was produced, which gave with water a magnificent rose-red solution; the bulk of the product of the reaction, however, was a black resin, which was only sparingly soluble in water, and gave a deep reddish-brown solution, which possessed the property of dyeing silk a beautiful salmon-pink. As no pure compounds could be separated from the products of the reaction, and the reaction itself seemed to be one of considerable complexity, the attempt to substitute chlorine for the oxygen atom in the carbonyl group of the lactone was abandoned.

The action of several other reagents was tried on the lactone. Heated with strong sulphuric acid at 200°, evolution of carbon dioxide began, and a small quantity of acetylacetone was produced. On cooling the mixture and pouring it into water, the original lactone crystallised out. If the heat is raised above 200°, the lactone is completely decomposed with evolution of carbon dioxide, sulphur dioxide, and other products, whilst a black charred mass remains in the flask.

With dilute sulphuric acid (25 per cent.), the lactone is at once decomposed. 1·30 grams were boiled with excess of the dilute sulphuric acid; 250 c.c. of carbon dioxide were at once evolved, and at the end of five minutes no further evolution of gas occurred. The residue contained nothing but acetylacetone and the sulphuric acid. The reaction appears, therefore, to be quantitative, and is expressed by the following equation:—

$$C_6H_6O_3 + H_2O = CH_3\cdot CO\cdot CH\cdot CO\cdot CH_3 + CO_2.$$

1·30 grams of the lactone of triacetic acid should give about 240 c.c. of carbon dioxide.

The lactone can be evaporated to dryness over the water-bath with strong nitric acid, without much change taking place; on the other hand, if it is first dissolved in strong sulphuric acid and the solution kept cold in a freezing mixture, the addition of a mixture of strong nitric and sulphuric acids causes no evolution of gas, but on pouring the liquid on to powdered ice, a nitro-compound separates as a flocculent precipitate. When recrystallised from glacial acetic acid, this forms yellow crystals melting at 210—212° (corr.).

On analysis:—

0·4045 gram substance gave 29·5 c.c. N at 758 mm. and 15° = 8·51 N.

	Calculated for $C_6H_5(NO_2)O_3$.	Found.
N	8·18	8·51

The lactone when warmed with hydriodic acid seems to be unacted on, as only traces of acetylacetone were noticed, and apparently the whole of the lactone could be recovered.

Heated at 100° with acetyl chloride and sodium acetate, it remains unchanged and therefore probably does not contain a hydroxyl group.

Action of Heat on the Ammonium Salt of the δ-Lactone of Triacetic Acid.

If the lactone is dissolved in strong aqueous ammonia and the salt heated on the water-bath, a crystalline substance very soon begins to separate, and if the mixture is evaporated to dryness and the residual salt heated to about 100°, the conversion into a new nitrogen compound is very nearly complete. The new compound, recrystallised from alcohol and water, melts at about 315° (330°, corr.); it then rapidly chars. When boiled with strong caustic soda, not a trace of ammonia is evolved. Heated with zinc-dust, it gives the pyrrol reaction with a pine splinter moistened with strong hydrochloric acid.

I. 0·2060 gram substance gave 0·4315 gram CO_2 and 0·1080 gram H_2O.

II. 0·1980 gram substance gave 0·4160 gram CO_2 and 0·1055 gram H_2O.

III. 0·2630 gram substance gave 26·2 c.c. N at 16° and 760 mm.

	Calculated for $C_6H_7NO_2$.	Found. I.	II.	III.
C	57·60	57·12	57·30	—
H	5·60	5·85	5·92	—
N	11·20	—	—	11·61

The reaction therefore is a simple one:—

$$C_6H_6O_3 + NH_3 = C_6H_7NO_2 + H_2O.$$

As the investigation of this new nitrogen compound is not yet completed, I shall reserve the results for a future communication.

LVII.—*Some Reactions of Dehydracetic Acid.*

By J. Norman Collie, Ph.D., F.R.S.E., University College, London.

During the last six months I have been working with large quantities of dehydracetic acid, and find that several important reactions of this interesting substance have hitherto escaped notice. I have therefore collected them and am induced to bring bring them before the

Society, as I think that they will be of considerable use to anyone who is working with dehydracetic acid.

Preparation.—In the preparation of dehydracetic acid, it is usually stated that when it is formed from ethylic acetoacetate, alcohol is the only other substance produced. This is quite incorrect, as the following numbers will show:—

From 1500 grams of ethylic acetoacetate, after passing through an iron tube heated to dull redness (see Oppenheim and Precht, *Ber.*, 9, 324), I obtained:—

	Grams.
Dehydracetic acid	450
Acetone, b. p. 57—61°	150
Acetone and alcohol, b. p. 60—78°	190
Alcohol, b. p. 78—80°	160
Residue, alcohol, water, and ethylic acetoacetate, b. p. above 80°	170
Carbon dioxide, ethylene, and loss	380
Total	1500

A large quantity of ethylene dibromide (b. p. 131—132°) was obtained by passing the gases evolved during the operation through bromine. This ethylene could not have been formed by the decomposition of the alcohol, for the temperature of the iron tube was too low to effect the change; its formation must therefore be accounted for by some other reaction. I think that it may, with considerable probability, be expressed as follows:—

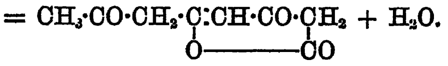
$$CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 = CH_3\cdot CO\cdot CH_2\cdot COOH + C_2H_4,$$

and the acetoacetic acid (diacetic acid), at the moment of formation, partly decomposes into acetone and carbon dioxide:—

$$CH_3\cdot CO\cdot CH_2\cdot COOH = CH_3\cdot CO\cdot CH_3 + CO_2,$$

and partly condenses to tetracetic acid and then to dehydracetic acid:—

$$\underset{\text{Diacetic acid.}}{2CH_3\cdot CO\cdot CH_2\cdot COOH} = \underset{\text{Tetracetic acid.}}{CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot COOH} + H_2O$$



$$= CH_3\cdot CO\cdot CH_2\cdot \underset{|}{C}{:}CH\cdot CO\cdot \underset{|}{C}H_2 + H_2O. \quad (O\text{———}CO)$$

δ-Lactone of tetracetic acid
or dehydracetic acid.

Various trials were made to produce dehydracetic acid by other reactions. Methylic acetoacetate gives large quantities of dehydracetic acid when passed through a hot tube. Ethylic ethylacetoacetate, however, does not yield a trace of dehydracetic acid, or any ethyl derivative of it, when similarly treated. Chloride of acetyl and acetic anhydride were also treated in various ways, such as passing through red-hot tubes, boiling with zinc chloride or aluminium chloride, but with negative results.

Properties.

Dehydracetic acid is volatile with steam to a considerable extent, and is also slightly decomposed with water into carbon dioxide and dimethylpyrone. In the evaporation, therefore, of a solution of the free acid, a large quantity is always lost. This conversion into dimethylpyrone is more conveniently carried out by boiling dehydracetic acid with ordinary fuming hydrochloric acid. First (*Annalen*, **257**, 272) prepares dimethylpyrone by heating dehydracetic acid in sealed tubes with ten times its weight of hydriodic acid of sp. gr. 1·5 for a day and a half at 150—160°, and states that dehydracetic acid is not attacked by sulphuric acid below 135° or by hydrochloric acid. I have shown elsewhere (p. 609) that sulphuric acid will change it into the δ-lactone of triacetic acid, and I find that if 50 grams of dehydracetic acid is boiled with strong hydrochloric acid, in about half an hour it is *totally decomposed*,

The reaction being as follows :—

$$C_8H_8O_4 + H_2O + HCl = C_7H_{11}O_3Cl + CO_2.$$

In a quantitative experiment, 2 grams of acid were boiled with hydrochloric acid, and yielded, after a short time, 250 c.c. of carbon dioxide. The amount demanded by the above equation is about 260 c.c.

After boiling dehydracetic acid with hydrochloric acid, the solution, on evaporation, yields magnificent groups of tabular crystals, much resembling those of creatinine. This compound was first obtained during an attempt to reduce dehydracetic acid with tin and hydrochloric acid; after the tin chloride and excess of hydrochloric acid had been removed, the concentrated solution deposited crystals which, on analysis, gave the following numbers :—

I. 0·4035 gram substance gave 0·6950 gram CO_2 and 0·238 gram H_2O.

II. 0·3385 gram substance gave 0·2730 gram AgCl.

	Calculated for $C_7H_{11}O_3Cl$.	Found.	
		I.	II.
C	47·06	46·97	—
H	6·16	6·55	—
Cl	19 88	—	19·95

The substance was, therefore, thought to be a hydrochloride of diacetylacetone, $C_7H_{10}O_3$. It does not, however, give any reaction with ferric chloride solution, whilst diacetylacetone gives a deep cherry-red, nor can diacetylacetone be extracted from the aqueous solution by evaporation. When it is dissolved in water and treated with oxide of silver, chloride of silver is precipitated, and the solution becomes neutral, and on extraction with chloroform dimethylpyrone can be obtained (m. p. 132°, and b. p. 248—250°). When distilled, it first gives hydrochloric acid and water, and then dimethylpyrone.

It melts at 83—85°, and its solution in water is strongly acid to litmus paper. It can be produced from diacetylacetone by dissolving it in hydrochloric acid and allowing the solution to evaporate, or by concentrating over the water-bath.

Dimethylpyrone, when dissolved in hydrochloric acid, and the solution evaporated, however, does not seem to yield this compound.

Barium Salt of Dehydracetic Acid.

This salt is of interest, because it appears to be a true salt of tetracetic acid, and not of the lactone (dehydracetic acid). If a warm solution of barium hydrate be added to dehydracetic acid, the acid dissolves, but almost at once a crystalline salt begins to separate, which gave the following numbers on analysis:—

The salt was dried at 110°.

I. 0·3720 gram salt gave 0·1680 gram $BaSO_4$. Ba = 26·55 per cent.

II. 0·4835 gram salt gave 0·2235 gram $BaSO_4$. Ba = 27·18 per cent.

	Calculated for		Found.
	$(C_8H_7O_4)_2Ba$.	$(C_8H_9O_3)_2Ba$.	Mean.
Ba..........	29·08	27·02	26·86

On treating the substance with hydrochloric acid, dehydracetic acid is precipitated.

A Copper Compound of Dehydracetic Acid.

If dehydracetic acid is added to a solution of copper acetate in excess of strong ammonia, after standing for some time, a beautiful pink salt crystallises out in microscopic needles. This salt is very stable, not being decomposed even when boiled with sulphuretted hydrogen, but if hydrochloric acid be added, it is at once changed into ammonium chloride, copper chloride, and dehydracetic acid.

On analysis:—

I. 0·3700 gram salt gave 22·8 c.c. of nitrogen at 16° and 768 mm.
II. 0·499 „ „ 31·5 „ „ 15° „ 763 „
III. 0·5545 „ „ 0·0785 gram copper oxide.
IV. 0·3465 „ „ 0·6480 gram CO_2 and 0·1470 gram H_2O.

	Calculated for $C_{24}H_{25}O_9N_3Cu$.	Found.			
		I.	II.	III.	IV.
C	51·24	—	—	51·00	—
H..........	4·45	—	—	4·71	—
N	7·47	7·28	7·37	—	—
Cu..........	11·21	—	—	—	11·29

The equation which accounts for the formation of the new compound would be:—

$$3C_8H_8O_4 + 3NH_3 + CuAc_2 = C_{24}H_{25}O_9N_3Cu + 2HAc + 3H_2O.$$

Action of Hydrocyanic Acid on Dehydracetic Acid.

These two substances seem to be without action on one another. Dehydracetic acid was warmed with a saturated alcoholic solution of hydrocyanic acid, and then allowed to stand for about three weeks; on evaporating the alcohol and hydrocyanic acid, the dehydracetic acid remained unchanged.

LVIII.—*Dibenzyl Ketone.*

By Sydney Young, D.Sc., Professor of Chemistry, University College, Bristol.

Dibenzyl ketone, $(C_6H_5{\cdot}CH_2)_2CO$, was prepared by Popow (*Ber.*, 6, 560) by the action of heat on calcium phenylacetate. The substance was obtained in crystals melting at 30°, and its boiling point was 320—321°. Calcium phenylacetate crystallises with 3 mols. H_2O, of which $2\frac{1}{2}$ mols. are expelled at 100°; the remaining water is not easy to remove completely, for the salt becomes viscous if the temperature be raised quickly to about 130° in an ordinary copper airbath, and in this condition the water is obstinately retained. When heated more strongly in the air, the salt darkens in colour, and evidently undergoes partial decomposition. In order to remove the water as completely as possible, the temperature should be raised very gradually from 100° to 130°.

A quantity of the dried calcium salt was first heated in a hard glass tube in a combustion furnace, a current of carbon dioxide being passed through the tube, and the temperature kept as low as possible. This method is, however, very tedious, and the product obtained was very far from pure; but by fractional distillation and crystallisation from ether, about 27 per cent. of the theoretical yield was obtained. The melting point of the pure product was 33·85°, and on distillation it boiled quite constantly.

In order, if possible, to discover some better method of preparation, the effect of heat on the calcium salt was more carefully studied. The salt, dried in the steam chamber, was placed in a bulb with a long neck, through which a current of carbon dioxide was constantly passed, and it was heated by the vapours of pure liquids, with the following results:—

At 130° water was expelled, but the salt did not melt.

At 150° more water was expelled, and the salt melted, forming a colourless, very viscous mass.

At 184° and 223° a very little water was expelled, and the salt frothed up slightly.

At 284° a slight turbidity, and a very little discoloration, was observed.

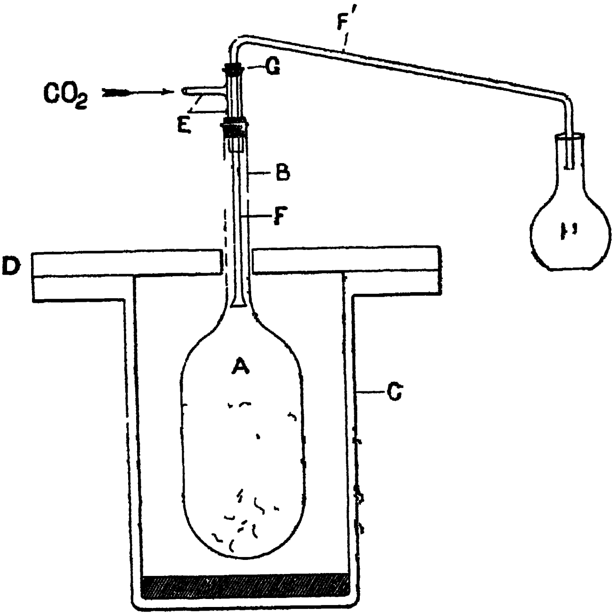
At 360° white fumes were evolved and condensed to a heavy oil, which solidified on the addition of a crystal of dibenzyl ketone. The quantity formed was very small, but after half-an-hour's heating the melted salt had become quite opaque.

At 446° the ketone came over freely, and condensed as a clear liquid, colourless at first, but gradually becoming yellow, orange, and finally brown, as the distillation proceeded. The residue in the bulb consisted of calcium carbonate, together with a little dark, oily substance.

From these results it appears that it is necessary to heat the calcium salt above 360°, but that a temperature of 450° should not be exceeded.

The apparatus finally adopted is shown in vertical section in the diagram.

The calcium salt, dried at 130°, was placed in the wide, cylindrical glass bulb A, sealed to the narrower tube B. This was heated in the flanged iron vessel, C, provided with the heavy iron cover D (this iron vessel had previously been employed by Dr. Richardson as a sulphur-bath, in his research on the dissociation of nitrogen peroxide). The tube B was provided with an indiarubber cork, through which the T-tube E passed. A piece of barometer tubing, FF′, enlarged conically at its lower end, passed through the T-tube and the tube B, and was attached to the T-tube by an ordinary cork, G,



the temperature being too high to admit of an indiarubber cork being employed The barometer tube was bent, as shown in the diagram, after the T-tube and the cork G had been placed in position. The vessel AB, containing the salt, was first placed in the bath, and the perforated iron cover passed over the tube B; the tubes E and F were then placed in position, and the vessel AB secured by means of a retort stand and clamp. The iron bath, containing sulphur, rested on a tripod, and was heated by a Bunsen burner below and a couple of burners at the sides. A slow current of dry carbon dioxide was passed constantly through the apparatus, entering the T-tube F, passing between the tubes B and F, and finally escaping through the tube FF′.

In this way, all vapour that was evolved from the calcium salt was forced into the barometer tube, where it condensed, and was carried into the receiver H.

The heavy iron cover D never became heated to the boiling point of sulphur, and acted as a very efficient condenser, the escape of sulphur vapour being extremely small, and causing no inconvenience.

This method possesses the following advantages:—

(1.) Larger quantities can be heated than by the ordinary method, from 40—50 grams of the crude ketone being obtained in each operation with the apparatus actually employed, and there seems no reason why a larger one should not give good results. (2.) The temperature does not rise above 450°, and serious loss, owing to decomposition of the ketone, is thus avoided. (3.) The condensed liquid is prevented, to a great extent, from flowing back into the hot bulb, and this seems to be of considerable importance, for the large surface of strongly heated calcium carbonate would otherwise cause a considerable amount of decomposition. (4.) The hot, condensed liquid does not come in contact with any cork or indiarubber. (5.) There is very little fear of breakage, for the bulb A is gradually and uniformly heated, and the hot liquid does not come in contact with any sealed joint, as in the ordinary distillation apparatus. (6.) A partial separation of the distillate into fractions is carried out in the preparation of the substance.*

1 kilogram of phenylacetic acid should give 772 grams of dibenzyl ketone. In the actual experiments, 928 grams of the acid (obtained from Kahlbaum) were converted into calcium salt and subsequently heated, but as the amount of acid was not far short of a kilogram, I have corrected all the weights of the ketone obtained to what they would have been if a kilogram had actually been employed.

The distillate was collected in each operation in four fractions: the first was nearly colourless, but contained some water; the colour of the second was pale-yellow, of the third brownish-yellow, and of the last a deep reddish-brown. The second fraction solidified almost completely, the third contained some liquid after cooling, the fourth gave a considerable crop of crystals, but the solidification was far from complete.

The results obtained (calculated for 1 kilo. of acid) are given below:—

Fraction.	I.	II	III.	IV.	Total.
Weight in grams ..	36·5	289·5	273·0	120·5	719·5
Melting point	not observed	29 5°	28·0°	not observed	—

The first fraction was then pressed between filter paper in a copying press; the second was gently warmed and the liquid poured off; the third and fourth were filtered by means of a filter pump. The quantities and melting points after this preliminary purification were as follows:—

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* It is possible that still better results might be obtained at a somewhat lower temperature with an air-bath of the form devised by Lothar Meyer.

Fraction.	I.	II.	III.	IV.	Total.
Weight	32·5	232·5	242·0	75·5	582·5
Melting point	32·6°	32·25°	31·4°	31·2°	—

The four fractions were melted together, a little ether added, and the ethereal solution allowed to crystallise slowly. Beautiful large crystals were thus obtained, and, after pouring off the mother liquor, these were melted again and recrystallised from ether, the process being repeated several times. Part of the ether from the mother liquors was in each case removed by distillation, fresh crops of crystals being thus obtained, and these were further purified by recrystallisation from ether.

The recrystallised product was finally distilled, and was found to boil quite constantly at 330·55° (corrected to 760 mm. at 0°). The melting point, obtained by immersing a thermometer in the solidifying liquid, was 33·9°.

The weight of ketone obtained in this manner without any fractional distillation was 404·5 grams, or 52·4 per cent. of the theoretical yield.

The filtrates from the original fractions III and IV, the liquid poured off from II, and the residual ethereal mother liquors were subjected to fractional distillation, and the purest fraction recrystallised from ether. In this way a further yield of 187 grams of the pure product, melting and boiling at the same temperature, was obtained.

The total amount of pure ketone obtained was thus 591·5 grams out of a possible 772 grams, or 76·6 of the theoretical yield.

The remaining distillates, after being pressed between filter paper, melted at 33·1° and weighed 26 grams.

The residues in the bulb A were treated with hydrochloric acid to dissolve the calcium carbonate (a little alcohol being added towards the end to complete the solution), and the dark, oily residues were separated from the solutions of calcium chloride. The total weight, after washing with water, and while still moist, was 77·5 grams.

On distillation, the oil yielded small quantities of toluene, a liquid boiling, after purification, at 226—227° (corrected), about 12 grams of undecomposed phenylacetic acid, a little dibenzyl ketone (fractionated with the larger quantity of ketone), and a tarry residue.

The liquid boiling at 226—227° was examined by Mr. R. M. Prideaux and Mr. G. L. Thomas in this laboratory, with the following results:—

Analysis of the Liquid.

	Observed.		Calculated for $C_{10}H_{12}O_2$.
Carbon..........	73·36	73·13	73·17
Hydrogen........	7·83	8 01	7·32
Oxygen..........	18·81	18 86	19·51

Vapour Density by V. Meyer's Method.

Observed, 81 6 and 83·3. Calculated for $C_{10}H_{12}O_2$, 82·0.

LIX.—*On the Vapour Pressures of Dibenzyl Ketone.*

By Sydney Young, D.Sc., Professor of Chemistry, University College, Bristol.

In order to obtain constant temperatures above 280°, the vapour of mercury boiling under known pressures may be employed, but there are serious objections to this substance, and it seems doubtful whether absolutely accurate results can always be obtained with it. Up to 306° benzophenone may be employed, and this substance is strongly recommended by Crafts (*Amer. J. Sci.*, 5), but the range of temperature above 280° is small.

It seemed probable that dibenzyl ketone might give good results, and I have therefore prepared some of this substance by a method described in the preceding paper.

The boiling point of dibenzyl ketone is 330·55° under normal pressure; there is thus a convenient range of temperature—just 50°—between the boiling points of this substance and of bromonaphthalene.

The ketone is a stable substance, for after several hours heating at temperatures between 260° and 330°, no alteration in the boiling point was observed. It is true that a little decomposition had taken place, for the ketone was no longer colourless, and on subsequent distillation the temperature, though very nearly constant for some time, did not remain so throughout. The rise of temperature was 0·3° after about three-fourths of the substance had distilled over; afterwards the rise was more rapid, and a little tarry liquid was left in the bulb. The product of decomposition possesses, however, a higher boiling point than the ketone, and was not present in sufficient quantity to affect the temperature of the vapour above the liquid while the measurements were being made. The first and second series of determinations were made with different samples of the ketone, which were afterwards mixed together, and a portion of this was employed for the third and fourth series. The last series of determinations was therefore made with a portion of the ketone which had been boiled under various pressures for several hours, but the results agreed perfectly with those previously obtained.

The low melting point, 33·9°, of the ketone is also convenient, whilst, on the other hand, the readiness with which it crystallises from ether greatly facilitates its purification. Dibenzyl ketone may therefore be recommended for obtaining constant temperatures between 280° and 330°.

In the determinations of the vapour pressures of the substance, temperatures from 230° to 280° were read on an ordinary thermometer, standardised by means of bromonaphthalene. For higher temperatures a mercury vapour pressure thermometer was employed.

In the first two series of determinations the liquid was boiled in a slightly modified distillation bulb, the neck of which was sufficiently long to allow of the whole of the mercury in the thermometer being heated by the vapour. The lower part of the neck of the distillation bulb was covered with asbestos, to reduce the loss of heat by radiation.

The apparatus employed for the higher temperatures was similar to that described by Dr. Ramsay and myself (Trans., 1885, **47**, 651). The tube in which the ketone was boiled was 510 mm. long, and 41 mm. in internal diameter. At each temperature from two to six readings were, as a rule, taken, and the mean results are given in the tables.

In calculating the temperatures, the vapour pressures of mercury determined by Ramsay and myself (Trans., 1885, **49**, 37) were first employed, but it seems probable that, owing to an error in Regnault's determination of the boiling point of sulphur, the vapour pressures of mercury, which at high temperatures depend on those of sulphur, require some alteration. The point is discussed in a paper on the Vapour Pressures of Mercury.

The temperatures under the heading "corrected" have been finally adopted.

The pressures are in millimetres of mercury at 0°, and the temperatures are those of an air thermometer.

EXPERIMENTAL RESULTS.

Temperatures with Ordinary Thermometer.

Series I.—Sample of ketone obtained by heating calcium phenylacetate in a combustion tube.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
230·55	60·3	249·1	105·6	270·35	191·7
232·85	64·95	253·1	118·7	274·45	213·5
236·05	71·5	257·85	136·1	278·0	234·2
240·2	81·15	262·55	155·0	—	—
244·3	91·8	266·6	173·25	—	—

Series II.—Sample of the ketone obtained by new method.

237·55	75·45	254·95	125·35	270·65	193·45
242·0	85·8	258·65	139·2	274·4	213·7
246·35	97·55	262·8	156·5	277·45	231·2
250 6	111·15	266·7	174 05	—	—

Temperatures with Mercury Vapour-pressure Thermometer. Series I.

Temp.	Corrected.	Pressure.	Temp.	Corrected.	Pressure.
260·65	260·8	147·9	293·55	293·4	338·3
265·8	265·8	169·75	303·3	303·0	422·3
270·25	270·3	192·25	317·4	316·85	570 8
276·95	276·85	227·5	330 8	330·1	746 45
284·65	284·55	276·0	—	—	—

Series II.

261 0	261·1	150·6	299·95	299·7	392·1
268·9	268·7	183 35	308·35	307 95	471·5
274·35	274·25	213·4	314·55	314·1	537·2
282·8	282 75	262·7	322·15	321·55	630·1
288·9	288·7	304·6	330·85	330·1	747·8

The agreement between the four series of results is very satisfactory.

The logarithms of the pressures were mapped against temperatures, and the logarithms of pressures corresponding to even temperatures read off. Constants for Biot's formula ($\log p = a + b\alpha^t$) were then calculated, and from these the pressures corresponding to definite temperatures—each 10° from 230° to 330°, and each degree from 280° to 332°—were calculated.

The constants for Biot's formula are—

$$a = 4{\cdot}75779,$$
$$b = -2{\cdot}981088 \quad \log b = 0{\cdot}4743748,$$
$$\log a = \bar{1}{\cdot}9980014,$$
$$t = t^\circ\,\text{C.} - 230.$$

The calculated pressures are given in the following tables:—

I.

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
230	59·80	260	144·90	290	313·3	320	613·2
240	81·45	270	189·65	300	396·0	330	752·0
250	109·35	280	245·20	310	495·2	—	—

II.

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
280	245·2	294	344·5	308	474·0	322	639·3
281	251·4	295	352·7	309	484·5	323	652·6
282	257·7	296	361·1	310	495·2	324	666·2
283	264·2	297	369·6	311	506·2	325	679·9
284	270·8	298	378·2	312	517·3	326	693·9
285	277·5	299	387·0	313	528·6	327	708·1
286	284·4	300	396·0	314	540·1	328	722·5
287	291·4	301	405·1	315	551·8	329	737·2
288	298·5	302	414·4	316	563·6	330	752·0
289	305·8	303	423·9	317	575·7	331	767·2
290	313·3	304	433·6	318	588·0	332	782·5
291	320·9	305	443·4	319	600·5	—	—
292	328·6	306	453·4	320	613·2	—	—
293	336·5	307	463·7	321	626·2	—	—

LX.—*The Vapour Pressures of Mercury.*

By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

IN the determinations of the vapour pressures of mercury (Ramsay and Young, Trans., 1886, 49, 37), the highest temperature was obtained by heating the metal with the vapour of boiling sulphur, and in calculating the results the boiling point of sulphur given by Regnault (*Mémoires*, vol. 26) was taken as correct. Callendar and Griffiths have, however, recently redetermined the boiling point of sulphur with an air thermometer, and have found it to boil at a temperature nearly 4° lower than Regnault did. Their experiments have evidently been carried out with great care, and they point out that Regnault himself did not place very great confidence in the values he obtained.

Again, the boiling point of mercury determined by Callendar and Griffiths by their platinum thermometer, calibrated by means of an air thermometer, is nearly 2° lower than that given in the paper referred to.

I have employed the vapour of mercury as a jacket in the determination of the critical temperatures and pressures of chlorobenzene and of stannic chloride (not yet published) and in both cases the temperature appeared to be rather too high. In the case of stannic chloride, constants could not be calculated for Biot's formula which would reproduce both the pressures at 240—280° (determined by means of bromonaphthalene) and those at 310 and 320°, in the determination of which mercury was employed. It has been pointed out in various papers by Ramsay and myself that errors in the determination of the vapour pressures of a substance may be discovered by comparing the absolute temperatures with those of a second substance at the same series of pressures. The ratios of the absolute temperatures mapped against the temperatures of one of the two substances should give a straight line, at any rate for a moderate range of pressure, and if there is pronounced curvature it may be concluded that the vapour pressures of one or other substance require correction. The existence of considerable errors in Regnault's vapour pressures of mercury and in Landolt's vapour pressures of the fatty acids was discovered in this way.

On the other hand, it may, of course happen that a straight line is obtained even when the determinations are faulty, for the errors may be of such a nature as to give a straight line somewhat different in direction from the true one. This appears to be the case with sulphur, for the ratios of the absolute temperatures, as determined by Regnault, to those of carbon bisulphide under equal pressures, do give a straight line when mapped against the temperatures of carbon bisulphide.

The ratios of the absolute temperatures of dibenzyl ketone to those of both water and benzene give very decided curves if the vapour pressures of mercury given in the paper referred to be taken as correct.

All these facts point to the conclusion that the vapour pressures of mercury based on Regnault's boiling point of sulphur are too low at high temperatures, in other words, that the boiling points are too high.

The calculations of the vapour pressures of mercury, made by Ramsay and myself, were based on the following experimental data:—

1. Direct determination of vapour pressures of mercury in a U-tube closed at one end and connected at the other with a gauge and barometer The tube, containing mercury, was heated with bromonaphthalene under atmospheric and reduced pressure, and with methyl salicylate under atmospheric pressure.

2. Regnault's determinations of the boiling point of mercury under atmospheric pressure.

3. Direct determinations of vapour pressure at the boiling point of sulphur in a special apparatus.

1. In the case of methyl salicylate there may be a small error, for this substance has not been found to give such good results as the other pure liquids (Ramsay and Young, Trans , 1885, 47, 640) and I have recommended the employment of quinoline in place of it (Trans., 1889, 55, 483).

The pressures at 270° and 280° with bromonaphthalene are in all probability very nearly correct, for this substance has been repeatedly used for heating purposes, and the results obtained do not point to the existence of any error, or at most an extremely small one at these temperatures

2. Regnault's boiling points of mercury are far from satisfactory, the difference between the highest and lowest results amounting to nearly 2°.

3. The determinations of the boiling point of sulphur, and also of mercury, by Callendar and Griffiths may probably be taken as the best yet obtained, and I have, therefore, made use of them in the new calculations.

On account of the possibility of error with methyl salicylate I have determined the vapour pressures of mercury with quinoline and with aniline, boiling under atmospheric pressure, by the same method as that previously employed. The results, each of which is the mean of a considerable number of readings, are given in the table below.

	Temperature.	Pressure.	Calculated from tables by Ramsay and Young.
Aniline..........	183·8	9 94 ± 0·083	9·80
Same with larger apparatus	183·7	9·85 ± 0·046	
Quinoline........	236·9	51·85 ± 0 06	52·30

These results show that at low temperatures the results given in the tables require very little alteration.

Ratios of the absolute temperatures of mercury to those of water at equal pressures were then calculated and mapped against the temperatures of water. The points so obtained fall very nearly on a straight line, and the absolute temperatures of mercury are reproduced very well by the following formula:—

$$R = 1{\cdot}6004 + 0{\cdot}000882t,$$

where R is the ratio of the absolute temperature of mercury to that of water at any pressure, and t is the temperature of water on the centigrade scale at the same pressure.

A comparison is given below of the temperatures of mercury given by this formula with the data obtained experimentally, including the boiling point of mercury determined by Callendar and Griffiths, and the results by Dr. Ramsay and myself with sulphur, recalculated on the basis of Callendar and Griffiths' boiling point of that substance.

Press.	Absolute temp. of water.	Ratio calculated from formula.	Calculated temp. of mercury.		Observed temp. of mercury.	Differences.	
			Absolute.	Cent.		Temp.	Press.
9·87	284·1	1·6102	457·45	184·45	183·75	−0·7	+0·23
34·4	304·5	1·6282	495·8	222·8	222·15	−0·65	+0·65
51·85	311·95	1·6348	509·95	236·95	236·95	0·0	0·0
124·35	329·2	1·6500	543·2	270·2	270·3	+0·1	−0·3
157·15	334·2	1·6544	552·9	279·9	280·2	+0·3	−1·1
760·0	373·0	1·6886	629·85	356·85	356·76	−0·09	+1·2
2896·9	415·25	1·7259	716·7	443·7	443·15	−0·55	+20·7
2904·5	415 35	1·7260	716·9	443·9	444·15	+0·25	−9·4

For temperatures between 236° and 444°, the results given by the above formula are very good; but at lower temperatures the vapour pressures given in the paper by Dr. Ramsay and myself agree rather better with the observed values.

The formula $R = 1{\cdot}6004 + 0{\cdot}000882t$ has been employed in calculating the temperatures of dibenzyl ketone, given in the tables in the paper on the vapour pressures of that substance under the heading "Corrected." The ratios of the corrected absolute temperatures of dibenzyl ketone to those of water at the same pressures give an approximately straight line, very much better than that obtained with the uncorrected values.

The temperatures of dibenzyl ketone given by the formula

$$R = 1{\cdot}5842 + 0{\cdot}0003283t$$

(where t is the temperature of water in centigrade degrees), are compared in the following table with those calculated by means of Biot's formula at the same pressures:—

Pressure.	Temperature.		Difference.
	Biot	From ratios.	
70	235·05	234·8	−0·25
100	246·9	246·9	0·0
150	261·25	261·25	0·0
200	272·05	272·45	+0·4
300	288·2	288·4	+0·2
500	310·45	310·55	+0·1
760	330·55	330·15	−0·4

The vapour pressures of mercury were recalculated for each 10° from 180° to 480°, and for each degree from 330° to 360° by means of the formula

$$R = 1{\cdot}6004 + 0{\cdot}000882t,$$

which may be converted into

$$t = \sqrt{1133{\cdot}8T' + 594055} - 1043{\cdot}75,$$

where t is the centigrade temperature of water corresponding to an absolute temperature, T', of mercury at the same pressure. The temperature of water, t, being calculated, it is only necessary to refer to a table of the vapour pressures of water to find the required pressure.

The results are given in the following tables:—

Table of Vapour Pressures of Mercury.—I.

T.	P.	T.	P.	T.	P.	T.	P.
180	8·41	260	96·46	340	559·1	420	2085·0
190	11·98	270	124·0	350	672·5	430	2402·5
200	16·81	280	157·8	360	803·7	410	2757·0
210	23·22	290	198·9	370	951 7	450	3150·5
220	31 64	300	248·6	380	1127·5	460	3586·0
230	42·56	310	308·0	390	1325·0	470	4067·0
240	56·55	320	378·5	400	1548·5	480	4596·0
250	74·26	330	461·7	410	1801·0	—	—

II.

T.	P.	T.	P.	T.	P.	T.	P.
330	461·7	338	538·4	346	625·1	354	722·7
331	470·8	339	548·6	347	636·7	355	735·7
332	480·0	340	559·1	348	648·4	356	749·0
333	489·3	341	569·7	349	660·4	357	762·3
334	498·8	342	580·4	350	672·5	358	775·9
335	508·5	343	591·3	351	684·8	359	789·7
336	518·3	344	602·4	352	697·3	360	803·7
337	528·3	345	613·7	353	709·9	—	—

NOTE BY WILLIAM RAMSAY, Ph.D., F.R.S.

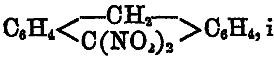
Professor Young has kindly sent me this note for revisal and criticism, on the ground that the former determinations were made by both of us, and that an alteration in the results should have the assent of both authors. I am convinced that, owing to the more accurate determination of the boiling point of sulphur at normal pressure made by Messrs. Callendar and Griffiths, the alterations in the numbers for the vapour pressures of mercury suggested in the foregoing paper are necessary. This affords another instance of the danger of accepting Regnault's data without criticism. In spite of the very great care he expended, the results of his investigations are by no means perfect, and further revision will doubtless lead to the discovery of other inaccuracies.

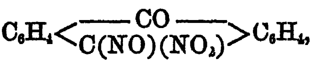
LXI.—*Action of Nitric Acid on Anthracene.*

By A. G. PERKIN.

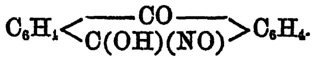
THE behaviour of anthracene towards nitric acid has been made the subject of repeated investigation at the hands of chemists, in every case with the same result, that anthraquinone, or one of its derivatives, is formed, instead of nitro-derivatives of anthracene. The reason for this lies in the fact that anthracene is more readily oxidised than nitrated, and, therefore, when treated with nitric acid, the hydrocarbon is at once converted into anthraquinone, and this, by the further action of the acid, then yields the well-known nitro-anthraquinones.

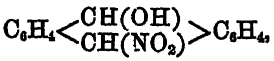
In the course of a series of experiments on anthracene derivatives, on which I have been engaged for some time, I had occasion to investigate again the action of nitric acid on this hydrocarbon, and I thus obtained a number of interesting results, a short account of which I beg to lay before the Society.

Several of the substances obtained in this investigation are closely allied to, and, in some cases, identical with, a series of derivatives obtained by Liebermann and Lindemann (*Ber.*, **13**, 1585) and Liebermann and Landshoff (*Ber.*, **14**, 467), and, in order to explain the connection between these somewhat complicated derivatives, I think it would be convenient to give a short summary of the results obtained by these chemists. When dihydroanthracene is treated with nitric acid in acetic acid solution, a colourless, crystalline substance, *hydranthracene nitrite*,  $C_6H_4<\begin{matrix}CH_2\\C(NO_2)_2\end{matrix}>C_6H_4$, is produced. This substance, when boiled with dilute potassium hydrate solution, is decomposed, with formation of *nitrosonitroanthrone*,

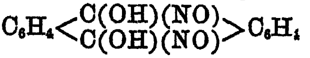


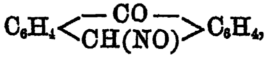
$$C_6H_4<\begin{matrix}CO\\C(NO)(NO_2)\end{matrix}>C_6H_4,$$

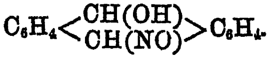
and nitroso-oxanthranol,  $C_6H_4<\begin{matrix}CO\\C(OH)(NO)\end{matrix}>C_6H_4$. A solution of anthracene in acetic acid, saturated with nitrogen trioxide, deposits, on standing, a precipitate of *anthracene nitrate*,



$$C_6H_4<\begin{matrix}CH(OH)\\CH(NO_2)\end{matrix}>C_6H_4,$$

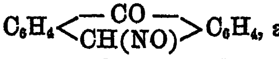
whereas, if nitrogen tetroxide is employed in the place of the trioxide, a substance $C_{14}H_{10}N_2O_4$ =  $C_6H_4<\begin{matrix}C(OH)(NO)\\C(OH)(NO)\end{matrix}>C_6H_4$ is produced, which is isomeric with hydranthracene nitrate.

Alkalis decompose anthracene nitrate, with formation of *nitrosoanthrone*,  $C_6H_4<\begin{matrix}CO\\CH(NO)\end{matrix}>C_6H_4$, and nitrosohydranthrone,



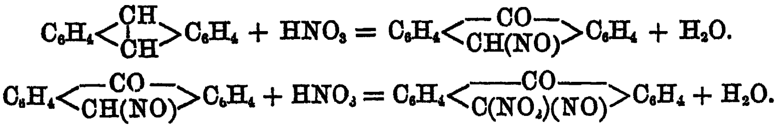
$$C_6H_4<\begin{matrix}CH(OH)\\CH(NO)\end{matrix}>C_6H_4.$$

The results obtained in my investigation of the action of nitric acid on solutions of anthracene are, briefly stated, the following:—

When a solution of anthracene in nitrobenzene is treated with fuming nitric acid, the principal products of the reaction are a beautiful, yellow substance $C_{14}H_8N_2O_4$, which melts at 292°, nitrosoanthrone,  $C_6H_4<\begin{matrix}CO\\CH(NO)\end{matrix}>C_6H_4$, and anthraquinone. The substance $C_{14}H_8N_2O_4$ was at first thought to be dinitroanthracene, as, although it has the same composition and similar properties to Liebermann and Landshoff's nitrosonitroanthrone, its melting point is 30° higher than they ascribed to the latter.

At a later stage in these experiments, it became necessary to prepare a considerable quantity of nitrosonitroanthrone, and, in purifying this carefully, a product was ultimately obtained which melted at 288—290°, and was, evidently, identical with the substance $C_{14}H_8N_2O_4$ obtained by me as described above.

It seems probable that, in the formation of nitrosonitroanthrone by the action of nitric acid on anthracene, nitrosoanthrone is first produced, and then, by the further action of nitric acid, it is converted into nitrosonitroanthrone, thus:—

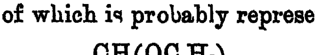


$$C_6H_4{<}\begin{matrix}CH\\|\\CH\end{matrix}{>}C_6H_4 + HNO_3 = C_6H_4{<}\begin{matrix}CO\\CH(NO)\end{matrix}{>}C_6H_4 + H_2O.$$

$$C_6H_4{<}\begin{matrix}CO\\CH(NO)\end{matrix}{>}C_6H_4 + HNO_3 = C_6H_4{<}\begin{matrix}CO\\C(NO_2)(NO)\end{matrix}{>}C_6H_4 + H_2O.$$

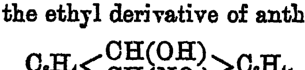
This hypothesis is supported by the fact that not only is nitrosoanthrone present in the product of the action of nitric acid on anthracene in nitrobenzene solution, but that this substance, when acted on by nitric acid, as is shown in the body of this paper, is almost quantitatively converted into nitrosonitroanthrone. Conversely, nitrosonitroanthrone, when subjected to the action of alkaline reducing agents, such as sodium sulphide, is reconverted into nitrosoanthrone.

Very interesting results were obtained in the study of the action of nitric acid on a solution of anthracene in a mixture of 2 parts of nitrobenzene and 3 parts of alcohol. In this case the reaction proceeds quite differently: a beautiful, colourless, crystalline substance is produced which has the composition $C_{16}H_{15}NO_3$ (= $C_{14}H_{10},C_2H_5NO_3$), and the constitution of which is probably represented by the formula



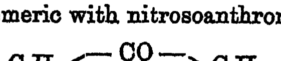
$$C_6H_4{<}\begin{matrix}CH(OC_2H_5)\\CH(NO_2)\end{matrix}{>}C_6H_4.$$

This substance, for which I propose the name *anthracene ethyl nitrate*, is probably the ethyl derivative of anthracene nitrate,

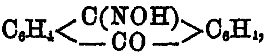


$$C_6H_4{<}\begin{matrix}CH(OH)\\CH(NO_2)\end{matrix}{>}C_6H_4.$$

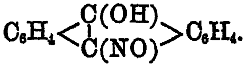
When boiled with hydrogen iodide solution, anthracene ethyl nitrate is readily decomposed, with formation of ethyl iodide and anthracene dihydride. Boiling alkalis convert it into a substance $C_{14}H_9NO_2$, which is isomeric with nitrosoanthrone,



$$C_6H_4{<}\begin{matrix}CO\\CH(NO)\end{matrix}{>}C_6H_4,$$

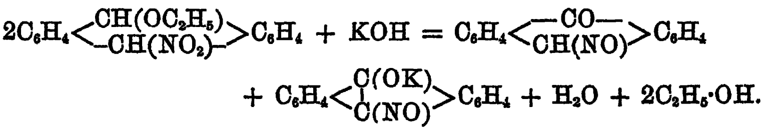


and also with isonitrosoanthraquinone, $C_6H_4{<}\genfrac{}{}{0pt}{}{C(NOH)}{-CO-}{>}C_6H_4$, and which, very probably, has the constitutional formula



$$C_6H_4{<}\genfrac{}{}{0pt}{}{C(OH)}{\overset{|}{C}(NO)}{>}C_6H_4.$$

The decomposition of anthracene ethyl nitrate by alkalis may therefore be represented by the following equation:—



$$2C_6H_4{<}\genfrac{}{}{0pt}{}{CH(OC_2H_5)-}{-CH(NO_2)-}{>}C_6H_4 + KOH = C_6H_4{<}\genfrac{}{}{0pt}{}{-CO-}{CH(NO)}{>}C_6H_4$$
$$+ C_6H_4{<}\genfrac{}{}{0pt}{}{C(OK)}{\overset{|}{C}(NO)}{>}C_6H_4 + H_2O + 2C_2H_5{\cdot}OH.$$

Pseudonitrosoanthrone.

This new substance, for which I propose the name pseudonitrosoanthrone, dissolves in alkalis, forming a deep orange-yellow solution; with acetic anhydride, it yields a well-characterised monacetyl derivative, $C_{14}H_8(OC_2H_3O)NO$. When treated with ammonia, or boiled with dilute sulphuric acid, anthracene ethyl nitrate is converted almost quantitatively into nitrosoanthrone.

A compound similar to anthracene ethyl nitrate is produced when methyl alcohol is substituted for ethyl alcohol in the above reaction. This has the composition $C_{14}H_{10}(CH_3{\cdot}NO_3)$, and is decomposed by alkalis exactly in the same way as the ethyl compound, yielding nitrosoanthrone and pseudonitrosoanthrone.

In studying these results by the side of those obtained by Liebermann and others, one cannot but be struck with the great reactive capacity of the centre portion of the anthracene molecule as distinguished from that of any other hydrocarbon which has as yet been investigated. Experiments are in progress by means of which it is hoped that this centre portion of the anthracene molecule may be to such a degree weakened that by some simple means a severance of the two benzene nuclei from the intervening portion may be brought about, in which case results of theoretical importance as bearing on the question of the constitution of anthracene might be expected.

Action of Nitric Acid on Anthracene in the Presence of Nitrobenzene.

In studying this action, finely powdered, pure anthracene was added in small portions at a time to a mixture of 1 part of fuming nitric acid, sp. gr. 1·5, and 2 parts of nitrobenzene. The anthracene quietly dissolved, and after a small quantity had been added, small, yellow needles began to appear in the solution. The addition of anthracene was continued until the whole had become of the consistency of a thin paste, but not longer, as in that case it was found that the resulting product was difficult to purify. During this addition, care was also taken to avoid rise of temperature. The whole was then thrown on to a funnel plugged with glass wool, and the filtrate placed aside for further investigation. The residue on the filter was washed two or three times with glacial acetic acid, then with alcohol, and dried. It consisted of a lemon-coloured mass of fine needles, and was further purified by one or two crystallisations from coal-tar naphtha with the aid of animal charcoal if necessary.

On analysis, numbers were obtained agreeing with the formula $C_{14}H_8N_2O_4$:—

I. 0 2091 gram substance gave 0·0599 gram H_2O and 0·4812 gram CO_2.

II. 0·1653 gram substance gave 0·0480 gram H_2O and 0·3818 gram CO_2.

III. 0·2394 gram substance gave 20·75 c.c. N.; temp. 8 5°; bar. 762·5 mm.

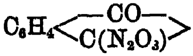
	Theory.	Found. I.	II.	III.
C	62·99	62·77	62·99	—
H	2·99	3·18	3·22	—
N	10·44	—	—	10·57

This substance may also be prepared: *a.*—By the addition of anthracene to a mixture of 1 part of fuming nitric acid and 2 parts of pyridine neutralised with nitric acid. The details of preparation are similar to those given above.

b.—By the addition of anthracene to cold nitric acid which had been purified by boiling with nitrate of urea. In this case the anthracene did not appear to dissolve in the acid, and the product remained suspended in the liquid as a yellow mass.

c.—By the addition of anthracene ethyl nitrate to a mixture of fuming nitric acid and nitrobenzene.

This substance, when prepared by either of these methods and very carefully crystallised from coal-tar naphtha, forms fine, long, yellow needles, often more than an inch in length, under the microscope showing a striated appearance resembling that of nitrate of potassium. It is less soluble in coal-tar naphtha than anthraquinone, a property which renders it easy of separation from the latter, which is always formed to some extent during the reaction. It is moderately soluble in hot aniline or nitrobenzene, and slightly soluble in hot alcohol, acetic acid, and benzene. It melts at 288—290°, and at higher temperatures, if carefully heated, sublimes unchanged with little or no carbonisation, but if superheated it suddenly decomposes with the formation of a cloud of black vapour, in this respect resembling the nitroanthraquinones. On exposure to sunlight, it slowly decomposes, the crystals being observed after some weeks to gradually curl up and become opaque, and on examination the product is found to consist of anthraquinone. Bromine has no action upon it in the cold, and it does not form a compound with picric acid. Cold sulphuric acid has no action upon it. When a solution of chromic acid was added to the substance suspended in glacial acetic acid, the mixture boiled for a few minutes, and water added, a white, crystalline precipitate was formed. This, after further purification, was obtained as white needles melting at 278°, and having all the properties of anthraquinone.

When added to strong fuming sulphuric acid, an energetic reaction took place. Water added to the product threw down a dirty white precipitate, which, after two or three crystallisations, appeared as white needles, consisting of pure anthraquinone. As stated in the introduction, this substance is evidently identical with *nitrosonitroanthrone*,  $C_6H_4<\begin{matrix}\text{—CO—}\\ C(N_2O_3)\end{matrix}>C_6H_4$, obtained by Liebermann and Landshoff by the action of alkalis on hydroanthracene nitrite.

The acid filtrate from the above substance, when treated with water and allowed to stand for a few days, became semi-solid owing to the separation of a crystalline compound. This was collected, pressed, and the residue crystallised two or three times from benzene. The product consisted of white needles melting at 278°, and having all the properties of anthraquinone.

In some cases when a larger quantity of anthracene than usual was added to a mixture of nitric acid and nitrobenzene without carefully cooling, a crystalline precipitate was obtained, and this was treated in the manner previously described. It was found to consist of a mixture of three substances, namely, nitrosonitroanthrone, anthraquinone, and a substance whose solubility in coal-tar naphtha was between the two. The yellow precipitate was first crystallised from this solvent to free it from anthraquinone, and the resulting crystalline mass very carefully fractionally crystallised from an excess of this solvent. The separation of these two substances presented no difficulty, as the point at which either commenced or finished crystallising was very sharply defined.

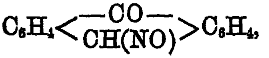
On analysis, the following numbers were obtained:—

I. 0·1400 gram substance gave 0·0570 gram H_2O and 0·3872 gram CO_2.

II. 0·1563 gram substance gave 0·0569 gram H_2O and 0·4302 gram CO_2.

These numbers give the percentages required for the formula $C_{14}H_9NO_2$.

	Theory.	Found.	
		I.	II.
C	75·24	75·03	75·43
H	4·03	4·04	4·04

This substance melts at 146° and is evidently identical with the nitrosoanthrone,  $C_6H_4<\begin{matrix}-CO-\\CH(NO)\end{matrix}>C_6H_4$, obtained by Liebermann and Lindemann (*Ber.*, **13**, 1585) by the action of alkalis on anthracene nitrate, $C_{14}H_{10}HNO_3$.

Action of Sodium Sulphide on Nitrosonitroanthrone.

When this was added to a boiling solution of sodium sulphide in alcohol, it quickly dissolved, forming a fine, red-violet solution, which, after a short digestion, gave no precipitate on the addition of boiling water. Hydrochloric acid, added to this solution, caused the formation of a heavy, brownish-yellow precipitate, which was collected washed, and dried. The resulting brownish-yellow powder was then digested with hot alcohol to which a few drops of aqueous potash had been added, and filtered. The filtrate, on cooling, deposited small, brownish-orange needles, which were collected, washed with hot alcohol and water, dried, and crystallised two or three times from acetic anhydride or alcohol. The yield of this substance was small, and from the residue insoluble in alcoholic potash no definite compound has been isolated.

On analysis, the following numbers were obtained :—

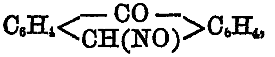
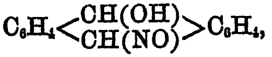
I. 0·1318 gram substance gave 0·0532 gram OH_2 and 0·3620 gram CO_2.

II. 0·1650 gram substance gave 0 0628 gram OH_2 and 0·4529 gram CO_2.

These numbers give percentages agreeing with the formula $C_{14}H_9O_2$.

	Theory.	Found.	
	$C_{14}H_9NO_2$.	I.	II.
C	75·34	74·91	74·80
H	4·03	4·48	4·22

As thus obtained, it forms long, orange-yellow needles, showing a striated appearance under the microscope. It is very soluble in benzene and carbon bisulphide, somewhat less so in acetic anhydride and acetic acid, and only moderately in alcohol. It melts to an orange coloured liquid at 146°. When added to cold sulphuric acid, a dirty green solution is produced which turns black when heated; the addition of water then throws down a black, carbonaceous precipitate. Fuming nitric acid attacks it violently with evolution of red fumes and formation of anthraquinone. When chromic acid is added to its solution in acetic acid, it reacts violently with formation of anthraquinone.

This substance is obviously identical with nitrosoanthrone,  $C_6H_4<\genfrac{}{}{0pt}{}{-CO-}{CH(NO)}>C_6H_4$, obtained by Liebermann and Lindemann (*Ber.*, 13, 1585) by treating anthracene nitrate or nitrite with alkalis. In the formation of this substance by the action of sodium sulphide on nitrosonitroanthrone, it is probable that an intermediate substance,  $C_6H_4<\genfrac{}{}{0pt}{}{CH(OH)}{CH(NO)}>C_6H_4$, is first produced which dissolves in alkalis with a violet colour, and is readily oxidised on exposure to air with formation of nitrosoanthrone. This is borne out by the fact that nitrosoanthrone, although itself insoluble in alkalis, readily dissolves in the presence of a reducing agent with the formation of a violet solution.

Action of Nitric Acid on Nitrosoanthrone in the presence of Nitrobenzene.

In order to afford additional proof of the constitution of nitrosonitroanthrone, the action of nitric acid on nitrosoanthrone was carefully investigated.

When nitrosoanthrone is added to a mixture of fuming nitric acid and nitrobenzene, it slowly undergoes change, without, however, passing into solution. The addition of this substance was continued until the whole became of a pasty consistency, and the product was then filtered through glass wool, the residue washed with acetic acid and alcohol, and dried. The lemon-coloured mass which, on examination, appeared as minute needles, was further purified by crystallisation from coal-tar naphtha.

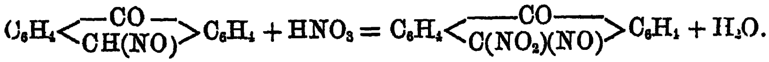
On analysis, the following results were obtained:—

0·1614 gram substance gave 0·0448 gram H_2O and 0·3717 gram CO_2.

These numbers give percentages agreeing with the formula required for nitrosonitroanthrone.

	Theory. $C_{14}H_8N_2O_4$.	Found.
C	62·69	62·80
H	2·99	3·08

As thus obtained, it consisted of long, orange needles sparingly soluble in boiling acetic acid and coal-tar naphtha. It melted at about 290—292°. The formation of nitrosonitroanthrone by the above reaction may be represented by the equation



$$C_6H_4<\begin{array}{c}CO\\CH(NO)\end{array}>C_6H_4 + HNO_3 = C_6H_4<\begin{array}{c}CO\\C(NO_2)(NO)\end{array}>C_6H_4 + H_2O.$$

Action of Nitric Acid on Anthracene in the presence of Alcohol and Nitrobenzene.

If finely divided anthracene is added to a mixture of 1 part of fuming nitric acid, 2 parts of nitrobenzene, and 3 parts of alcohol by volume, it slowly dissolves in the cold, but much more readily if very gently heated.

In studying this reaction, the addition of anthracene was continued until a sample of the product set to a pasty mass of crystals on cooling. The whole was then rapidly filtered to free it from any traces of undissolved anthracene, the solution thoroughly cooled, and the crystals which separated collected, washed two or three times with a little alcohol, and strongly pressed. It was then further purified by two or three crystallisations from alcohol.

On analysis, the substance dried at 60° gave the following numbers :—

I. 0·2816 gram substance gave 13·1 c.c. N; $t = 12°$; bar. 740 mm. 0·1745 gram substance gave 0·0913 gram H_2O and 0·4580 gram CO_2.

II. 0·1557 gram substance gave 0·0770 gram H_2O and 0·4090 gram CO_2.

III. 0·1197 gram substance gave 0·0602 gram H_2O and 0·3138 gram CO_2.

IV. 0·1737 gram substance gave 0·0870 gram H_2O and 0·4577 gram CO_2.

V. 0·1664 gram substance gave 0·0826 gram H_2O and 0·4378 gram CO_2.

These numbers give percentages agreeing with the formula $C_{14}H_{10},C_2H_5NO_3$.

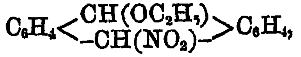
	Theory for $C_{14}H_{10},C_2H_5NO_3$.	I.	II.	III.	IV.	V.
C	71·4	71·58	71·64	71·49	71·87	71·75
H	5·6	5·81	5·49	5·59	5·56	5·51
N	5·2	5·40	—	—	—	—

The determination of the molecular weight of this substance by

Raoult's method gave the following numbers, agreeing fairly well with the formula $C_{14}H_{10},C_2H_5NO_3$.

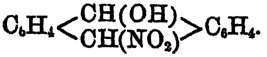
Substance taken	1·0422 grams.
Acetic acid „	75·6 „
Melting point of the acetic acid......	14·75° C.
„ the mixture........	14·53 „
Depression of the melting point......	0·22 „
Molecular weight of the substance found from the above data	244.
Theory for $C_{14}H_{10},C_2H_5NO_3$	269.

As stated in the introduction, this new substance is a compound of anthracene with the elements of ethyl nitrate, and from a study of its properties it is probable that it has the constitution



$$C_6H_4<\begin{matrix}CH(OC_2H_5)\\-CH(NO_2)-\end{matrix}>C_6H_4,$$

in which case it might be looked upon as the ethyl derivative of Liebermann's anthracene nitrate, which probably has the constitution



$$C_6H_4<\begin{matrix}CH(OH)\\CH(NO_2)\end{matrix}>C_6H_4.$$

Anthracene ethyl nitrate crystallises from alcohol in flat, white, glistening needles, which are readily soluble in benzene and chloroform, moderately so in alcohol and acetic acid. It melts at about 160° to a yellow liquid, and slightly above this point it decomposes with rapid evolution of nitrous fumes and formation of anthraquinone. This decomposition takes place slowly at temperatures below 100°, and on boiling with alcohol, acetic acid and other solvents, nitrous fumes are slowly given off and the solution becomes yellow. It is therefore necessary, when purifying this substance by recrystallisation, to conduct the operation as rapidly as possible, otherwise the product is with difficulty obtained in a colourless condition. When exposed over sulphuric acid in a vacuum, anthracene ethyl nitrate is sometimes very rapidly converted into a gummy, yellow mass. Dissolved in acetic acid and treated with chromic acid, it is converted into anthraquinone. Cold fuming nitric acid also converts it into this substance.

With a mixture of nitric acid and nitrobenzene, it behaves similarly to anthracene, nitrosonitroanthrone being formed, as was proved by the following analysis:—

0·1256 gram substance gave 0·0362 gram H_2O and 0·2888 gram CO_2.

	Theory for $C_{14}H_8N_2O_4$.	Found.
C	62·69	62·71
H	2·99	3·22

When boiled with strong aqueous potash, anthracene ethyl nitrate dissolves, forming a brownish-yellow solution, which, if concentrated, sets to a mass of brownish-yellow needles on cooling. The crystals dissolve in hot water, forming a yellow solution which, on the addition of acids, gives a white precipitate of a new substance which will be described below.

The solution of anthracene ethyl nitrate is coloured intensely yellow on the addition of ammonia, and, on cooling, orange-red needles are deposited. These were collected, washed with alcohol, and recrystallised from this solvent.

The analysis gave the following results:—

I. 0·1884 gram substance gave 0·0730 gram H_2O and 0·5197 gram CO_2.

II. 0·2704 gram substance gave 14·7 c.c. N; $t = 16°$; bar. = 742 mm.

	Theory for $C_{14}H_9NO_2$.	Found.
C	75·3	75·3
H	4·03	4·3
N	6·27	6·37

This substance melted at 146°, and showed all the properties of nitrosoanthrone.

The same decomposition takes place when anthracene ethyl nitrate in alcoholic solution is treated with pyridine and other bases, boiled in acetic acid solution with a few drops of sulphuric acid, or reduced with sodium sulphide.

Action of Alkalis on Anthracene Ethyl Nitrate.

Anthracene ethyl nitrate is readily decomposed by boiling with alcoholic potash with formation of a new substance possessing pronounced phenolic properties.

In studying this decomposition, anthracene ethyl nitrate was added to boiling dilute alcoholic potash. It rapidly dissolved, forming a dark-brown solution, and the decomposition was complete as soon as a small quantity taken out gave only a slight precipitate on diluting with water. On adding hydrochloric acid to the well-cooled product, a bulky, light-yellow precipitate was thrown down. This was collected, washed well with water, and dissolved in boiling very dilute aqueous potash. On cooling under the tap, a small quantity of a brownish substance was deposited, which was collected, and will be referred to later.

Hydrochloric acid was added to the filtrate, and the whitish precipitate redissolved in potash, and repeatedly treated in this manner until nothing was deposited on cooling. The resulting white, amorphous product was purified by two or three crystallisations from alcohol or benzene, and analysed with the following result:—

I. 0·1542 gram substance gave 0 0638 gram OH_2 and 0·4294 gram CO_2.

II. 0·1468 gram substance gave 0·0558 gram OH_2 and 0·4038 gram CO_2.

These numbers give percentages agreeing with the formula $C_{14}H_9NO_2$.

	Theory. $C_{14}H_9NO_2$.	Found. I.	Found. II.
C	75·3	75·29	75·02
H	4·03	4·59	4·20

This substance, which I propose to call pseudo-nitrosoanthrone, is moderately soluble in alcohol, from which it crystallises in minute groups of needles, more sparingly in benzene. It melts at about 224—225° with decomposition and evolution of nitrous fumes. The residue, on examination, was found to consist of anthraquinone. It can be crystallised from such solvents as acetic acid with but slight decomposition if the operation is rapidly performed. otherwise, after short contact with the boiling solvent, nitrous fumes are rapidly evolved and anthraquinone is formed. Chromic acid and cold nitric acid oxidise it readily to anthraquinone. It dissolves readily in alkalis, forming orange-yellow solutions. Cold sulphuric acid dissolves it with a yellow colour. When boiled with acetic anhydride, and the mass allowed to cool, colourless needles are deposited resembling anthraquinone in appearance. These were collected, purified by recrystallisation from alcohol, and analysed with the following result:—

I. 0·1535 gram substance gave 0 0592 gram OH_2 and 0·4060 gram CO_2.

II. 0·1872 gram substance gave 0·0720 gram OH_2 and 0·4960 gram CO_2.

III. 0·1516 gram substance gave 0·0591 gram OH_2 and 0 4032 gram CO_2.

IV. 0·1718 gram substance gave 0 0684 gram OH_2 and 0 4564 gram CO_2.

	Theory. $C_{14}H_8NO_2,C_2H_3O$.	Found. I.	II.	III.	IV.
C..........	72·45	72·1	72·26	72 2	72·44
H	4·15	4·2	4·27	4·3	4·42
N	5 28	—	—	—	—

This substance which, as the analyses show, is acetylpseudonitrosoanthrone, melts at 153—154°. It is moderately soluble in alcohol and acetic acid, very soluble in acetic anhydride. It is insoluble in dilute alkalis in the cold, but dissolves readily on warming, forming an orange solution. At high temperatures, or on boiling with a solvent of high boiling point, it gives off nitrous vapours, and is converted into anthraquinone. Chromic acid and nitric acid oxidise it to anthraquinone.

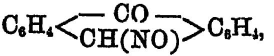
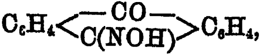
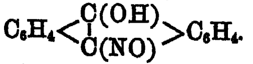
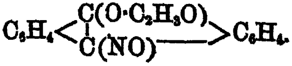
The brownish substance, after two or three crystallisations from alcohol, was obtained in long needles. Analysis:—

I. 0·1282 gram substance gave 0·0518 gram H_2O and 0·3524 gram CO_2.
II. 0·2195 gram substance gave 11·3 c c. N; $t = 16°$; bar. = 760 mm.

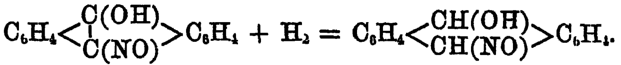
These numbers give percentages agreeing with the formula $C_{14}H_9NO_2$.

	Theory. $C_{14}H_9NO_2$.	Found. I.	II.
C	75·3	74·97	—
H	4·03	4·45	—
N	6·28	—	6·00

This substance has therefore the same composition as nitrosoanthrone, with which it is in every respect identical. It melts at 146°, crystallises in the same way, and shows all the properties of this substance.

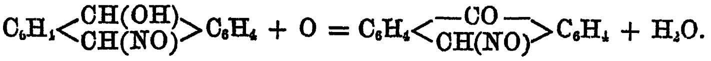
As stated in the introduction, pseudonitrosoanthrone is isomeric with nitrosoanthrone,  $C_6H_4<\genfrac{}{}{0pt}{}{—CO—}{CH(NO)}>C_6H_4$, and with isonitrosoanthraquinone,  $C_6H_4<\genfrac{}{}{0pt}{}{—CO—}{C(NOH)}>C_6H_4$, and it therefore probably has the constitution  $C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{C(NO)}>C_6H_4$. This formula accounts for the phenolic nature of the substance, and the fact that it forms an acetyl compound, which latter would be represented by the formula  $C_6H_4<\genfrac{}{}{0pt}{}{C(O{\cdot}C_2H_3O)}{C(NO)}>C_6H_4$.

The production of nitrosoanthrone by the reducing action of sodium sulphide may be represented thus :—

(1.) 

$$C_6H_4<\begin{matrix}C(OH)\\ |\\ C(NO)\end{matrix}>C_6H_4 + H_2 = C_6H_4<\begin{matrix}CH(OH)\\ CH(NO)\end{matrix}>C_6H_4.$$

Unstable intermediate substance.

(2.) 

$$C_6H_4<\begin{matrix}CH(OH)\\ CH(NO)\end{matrix}>C_6H_4 + O = C_6H_4<\begin{matrix}—CO—\\ CH(NO)\end{matrix}>C_6H_4 + H_2O.$$

Nitrosoanthrone.

Action of Hydrogen Iodide on Anthracene Ethyl Nitrate.

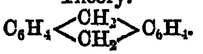
In studying this action, 5 grams of anthracene ethyl nitrate was mixed with 50 c.c. of aqueous hydrogen iodide (sp. gr. 1·96), and distilled gently from a retort. The dark-coloured distillate, on mixing with water, deposited a quantity of a heavy liquid, which was mechanically separated, mixed with water containing a trace of sulphurous acid, and the whole distilled. The heavy oil which separated from the aqueous distillate was collected, dried over calcium chloride, and distilled from a small Wurtz flask. It showed the boiling point of ethyl iodide (72°), with which it was identical, as the following analysis shows :—

0·1070 gram of substance, heated at 180° with nitric acid and nitrate of silver, gave 0·1608 gram AgI = 81·2 I per cent. Theory, C_2H_5I = 81·4 I per cent.

The residue in the retort was mixed with water and sufficient sulphurous acid to remove excess of iodine, the brownish-coloured substance collected, well washed with water, dried on a porous plate, and recrystallised from alcohol.

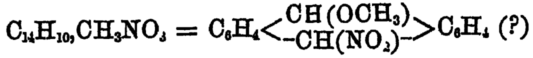
In this way, beautiful plates were obtained which melted at 106—108°, and showed all the properties of dihydroanthracene. Analysis :—

0·1634 gram substance gave 0·1004 gram H_2O and 0·5592 gram CO_2.

	Theory.  $C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>C_6H_4.$	Found.
C	93·33 per cent.	93·33 per cent.
H.........	6·66 „	6·83 „

This experiment shows, therefore, that anthracene ethyl nitrate, when boiled with aqueous hydrogen iodide, is decomposed into dihydroanthracene and ethyl iodide, most of the nitrogen being evolved as nitrous fumes.

Anthracene Methyl Nitrate,



$$C_{14}H_{10},CH_3NO_3 = C_6H_4<\begin{matrix}CH(OCH_3)\\ -CH(NO_2)-\end{matrix}>C_6H_4\ (?)$$

This substance is produced in a similar manner to the ethyl compound already described, to which it also bears the greatest resemblance. It crystallises from alcohol in glittering plates which melt at about 183° with decomposition and formation of anthraquinone. The analysis gave the following results:—

	Theory. $C_{14}H_{10},CH_3NO_3$.	Found.
C........	70·59 per cent.	70·36 per cent.
H........	5·10 ,,	5·39 ,,

Anthracene methyl nitrate is decomposed by alkalis, yielding a mixture of nitrosoanthrone and pseudonitrosoanthrone. The latter melted at 224—225°, the acetyl derivative at 153°, and in its properties was found to be exactly similar to the compound obtained by the action of alkalis on anthracene ethyl nitrate.

LXII.—*Researches on the Terpenes.*

On Camphene.

By J. E. Marsh, M.A., Balliol, and J. A. Gardner, Magdalen College.

This paper contains an account of our researches on camphene with regard to its preparation, products of oxidation, and substitution derivatives.

Of all the terpenes, camphene seems to us to possess the greatest amount of interest on account of its perfectly definite character as a single substance and not a mixture, of its relatively stable nature, of its capacity for giving substituted rather than additive compounds, and of its close relation to camphor. There appears to be no reason why the derivatives of camphene should not be as fruitful a subject of study as have been those of benzene.

Production of Camphene.

Our method of obtaining camphene is essentially that of Wallach as modified by Marsh and Stockdale (Trans., 1890, 57, 961), whereby along with camphene we obtain acetate of borneol. Instead, however, of employing sealed glass tubes for heating the mixture of turpentine hydrochloride, acetate of potash, and acetic acid, we use a large copper autoclave, which is not attacked by the acetic acid. By means of this, a large quantity of material can be operated upon at once. For heating the autoclave, we have found it convenient to use a bath of pitch, which can readily be heated to 250°, the temperature required, without danger, smell, or inconvenience. The crude camphene obtained is separated from the other product and from unaltered hydrochloride of turpentine, partly by distillation in steam. On rectifying, it at once solidifies in the cold.

Oxidation of Camphene.

Riban states that when camphene is oxididised by the "classical mixture" of potassium dichromate and sulphuric acid, it yields camphor. We have not, however, found this method suitable for preparing camphor. From 17 grams of camphene, after 18 hours boiling with 57 grams of dichromate, 70 grams sulphuric acid, and 140 grams of water, we recovered 12 grams of a solid, which certainly had the smell of camphor, but proved on distillation to be unaltered camphene, from which it would appear that part of the camphene is profoundly attacked by the oxidising mixture leaving the remainder unaltered.

By oxidising camphene with nitric acid, we have obtained some compounds of interest, but neither camphor nor any of its oxidation products.

Fuming nitric acid does not form a nitro-derivative, but acts violently on camphene with evolution of red fumes.

To oxidise camphene, we employ for every 20 grams of the substance 400 c.c. of dilute nitric acid. The camphene is heated in a matrass on the water-bath at first with 133 c.c. of acid of sp. gr. 1·42 and 133 c.c. of water. After the first action slackens, a second 133 c.c. of acid is added, and the whole heated until red fumes cease to be evolved. The liquid is then poured out into a dish and evaporated to a small bulk. On cooling, it sets to a mass of crystals. These are separated from the syrupy mother liquor and recrystallised, preferably from ether. A small quantity of a white powder is left undissolved by the ether, and is also insoluble in water. It and the syrupy mother liquor have been reserved for a further examination. The crystals obtained from the ether solution consist of a new acid of the formula $C_{10}H_{14}O_6$, which we call *camphoic acid.*

Camphoic Acid.

This new acid forms colourless crystals melting at 184—185° with decomposition. On analysis, it gave:—

	Found.	Calculated for $C_{10}H_{14}O_6$.
Carbon	51·6	52·1
Hydrogen	6·1	6·0

The barium salt was obtained in crystalline form, very soluble in water. It gave:—

	Found	Calculated for $BaC_{10}H_{12}O_6$.
Barium	35·3	35·8

From this it would appear to be dibasic, but the barium salt is acid to test paper, and the behaviour of the acid in other respects showed it to be *tribasic*, as will be seen later in considering the action of heat upon it.

We thus have the series of acids derived from camphor,

Campholic, monobasic	$C_{10}H_{18}O_2$.
Camphoric, dibasic..............	$C_{10}H_{16}O_4$.
Camphoic, tribasic	$C_{10}H_{14}O_6$.

Distillation of Camphoic Acid.—When camphoic acid is heated under ordinary pressure, it first melts, then loses carbonic anhydride and water, and distils at about 300° yielding the anhydride $C_9H_{12}O_3$ of a new acid which we call *camphopyric acid.* A very small residue is left in the retort.

Camphopyric Anhydride.—The distillate, when crystallised from alcohol, gives fine needle-shaped crystals closely resembling the anhydride of camphoric acid. They melt at 178—179°, and give on analysis:—

	Found.	Calculated for $C_9H_{12}O_3$.
Carbon	63·8	64·2
Hydrogen	7·3	7·1

Camphopyric Acid.—The anhydride was dissolved in hot caustic soda, and the acid precipitated by hydrochloric acid. It was recrystallised from water, and forms colourless, flaky crystals which melt at 209°, and give on analysis:—

	Found.	Calculated for $C_9H_{14}O_4$.
Carbon	57·83	58·06
Hydrogen	7·78	7·53

The barium salt is very soluble in water, and crystallises on evaporation in silky, white tufts. It appears to retain water of crystallisation even when heated in an air-bath to over 120° :—

	Found.	Calculated for	
		$BaC_9H_{12}O_4$.	$BaC_9H_{12}O_4 + H_2O$.
Barium (1)	40·2	42·9	40·4
„ (2)	40·6	—	—

Camphopyric acid is, therefore, dibasic, and the next lower homologue of camphoric acid, $C_{10}H_{16}O_4$, the anhydrides of the two acids being indistinguishable in appearance. It is interesting in this connection to note that camphopyric acid gives a fluoresceïn, whilst camphoric acid does not. When the former acid is heated with resorcin and a few drops of strong sulphuric acid, the melt gives with caustic soda a pink solution with a strong green fluorescence.

If then camphoric acid is represented, as has been proposed by one of us, as a substituted glutaric acid, $C_5H_{10}<\begin{array}{l}CH{\cdot}CH_2{\cdot}COOH\\ |\\ CH{\cdot}COOH\end{array}$, it is not improbable that camphopyric acid is the corresponding substituted succinic acid $C_5H_{10}<\begin{array}{l}CH{\cdot}COOH\\ |\\ CH{\cdot}COOH\end{array}$, the substituted succinic acids giving, as is known, fluoresceïns. Camphoic acid itself would then be represented as $C_5H_{10}<\begin{array}{l}C(COOH)_2\\ |\\ CH{\cdot}COOH\end{array}$.

Isocamphopyric Acid.—Camphopyric anhydride is not the sole product of the distillation of camphoic acid. There is obtained, mixed with the anhydride, an acid which is isomeric with camphopyric acid. It may be separated from the anhydride either by means of alcohol, in which it is much more soluble than the latter, or by treating the crude distillate in the cold with a slight excess of a solution of carbonate of soda, which dissolves the acid and leaves the anhydride. The acid is then precipitated from the solution of its sodium salt by hydrochloric acid, and crystallised from water. It separates from the hot aqueous solution as an oil which afterwards solidifies to a mass of crystals. The crystals form hard granules, are very different from the soft, flaky crystals of camphopyric acid. The melting point is near 160°, but was not always obtained quite constant, the substance probably containing a little of the isomeric acid. Its analysis gave :—

	Found.	Calculated for $C_9H_{14}O_4$.
Carbon	57·68	58·06
Hydrogen	8·19	7·53

When this acid is distilled, it is partly converted into camphopyric anhydride, but appears chiefly to distil unchanged. The recovered acid has now a sharper melting point, softening at 153° and melting at 157°.

The relationship of these two camphopyric acids obviously recalls that of the cis- and trans-camphoric acids, and should the analogy be subsequently confirmed we would propose a similar nomenclature. The isomeric change is, however, much less readily brought about in this case than in that of the camphoric acids, and we have been unable to convert camphopyric acid into isocamphopyric acid by means of the acid chloride, as was effected in the case of cis-camphoric acid (*Proc. Roy. Soc.*, 47, 7).

Action of Pentachloride of Phosphorus on Turpentine.

Pentachloride of phosphorus does not act on turpentine in the cold, but on heating to about 60° in a water-bath the action sets in with great violence, and with evolution of hydrogen chloride. We have not completed our study of the reaction, but among the products there appears to be formed, besides cymene, a crystalline dichloro-derivative melting at 170°.

Action of Pentachloride of Phosphorus on Camphene.

In the hope of obtaining chloro-substituted derivatives of camphene, we subjected this substance to the action of the same reagent.

Camphene was heated on a sand-bath with phosphorus pentachloride, phosphorus trichloride being used as a solvent, in a flask with reflux condenser, care being taken to exclude moisture. The whole was kept boiling for two or three days. The action was at no time violent. Hydrogen chloride was slowly evolved, and when this evolution ceased, the product of the reaction was distilled under diminished pressure.

The above was the general method of procedure, which varied in detail in some cases. Thus oxychloride of phosphorus was used as a solvent instead of the trichloride, or the product was poured into water instead of being distilled under diminished pressure.

In no case, however, could a chloro-derivative of camphene be isolated in any quantity in the pure state, though indication was obtained that such products were formed. The principal substance separated was a chlorophosphorus derivative of camphene of the formula $C_{10}H_{14}PCl_3$. It was found that phosphorus trichloride alone had little or no action on camphene, almost the whole of the latter being recovered unaltered after 20 hours heating with $1\frac{1}{2}$ mols. PCl_3.

Camphene and phosphorus pentachloride, in the proportion of 2 : 3 mols., were heated with a little phosphorus trichloride as a solvent for three days on the sand-bath. The phosphorus trichloride was then distilled off and the remainder fractionally distilled under diminished pressure. The chief part was obtained boiling between 160° and 170°, of which the fractions

$$\left.\begin{array}{l} a,\ 160\text{—}166^\circ \\ b,\ 166\text{—}168^\circ \\ c,\ 168\text{—}170^\circ \end{array}\right\} 17\text{—}18 \text{ mm. pressure,}$$

were kept separate.

Part of fraction *b* solidified on standing, and the remainder also when a small crystal from the solidified portion was introduced into it. The phosphorus and chlorine were determined in this fraction—

	Found.	Calculated for $C_{10}H_{11}PCl_3$.
Phosphorus	11·7 per cent.	11·4
Chlorine	38·5 „	39·2

Action of Water on the Compound.—In order to determine the nature of the above compound, we have studied the action of water, or rather of dilute caustic soda, upon it, from which it appeared that two-thirds of the chlorine was eliminated, and a mono-basic phosphine acid produced. The method of procedure was as follows:—

A small, weighed quantity of the substance was treated with a hot, dilute, standard solution of caustic soda in slight excess. When the reaction was complete, ascertainable by the whole, except a mere trace, going into solution, the excess of soda was neutralised by standard nitric acid. In this way the amount of soda neutralised by the substance was determined. The whole liquid was then made up to a known volume (250 c.c.), and the chlorine estimated in an aliquot part of the solution by means of a standard solution of silver nitrate, using chromate of potash as an indicator.

It was found that 1 mol. of $C_{10}H_{14}PCl_3$ required 3 mols. of NaHO for neutralisation, and that two-thirds of the total chlorine was precipitable by silver nitrate. This corresponds with the reaction

$$C_{10}H_{14}PCl_3 + 2H_2O = \underset{\text{Monobasic.}}{C_{10}H_{14}ClPO_2H_2} + 2HCl.$$

Experiment:—

0·2435 gram of substance was dissolved in 25 c.c. standard caustic soda (1 c.c. = 0·008 gram NaHO). The solution required 11·1 c.c. standard nitric acid (1 c.c. HNO_3 = 1 c.c. NaHO) for neutralisation. The whole solution was then made up to 250 c.c., of which 50 c.c. require 14·18 c.c. (mean) of standard silver nitrate (1 c.c. = 0·0085 gram $AgNO_3$). Hence

	Found.	Calculated.
1 mol. substance requires...	3·08	3 00 mols. NaHO.
P. c. chlorine as NaCl......	26·1	26·1

The original compound is thus chlorocamphenyl phosphorus chloride, $P\left\{\begin{array}{l}C_{10}H_{14}Cl\\ Cl\\ Cl\end{array}\right.$, which, acted upon by water, gives chlorocamphenylphosphorous acid, $P\left\{\begin{array}{l}C_{10}H_{14}Cl\\ OH\\ OH\end{array}\right.$. The above method of analysing the chloride volumetrically has been employed frequently in this laboratory for other and simpler acidic chlorides, notably by Mr. R. E. Hughes, of Jesus College, in his investigation of cinnamyl compounds (Proc., **91**, 70), and has been found to be perfectly trustworthy.

NOTE.

Professor Wallach (*Annalen*, **264**, 6) finds fault with Mr. Stockdale and myself as to our method of preparing camphene, and states that the materials should not be heated above 200°, since camphene itself undergoes decomposition above that temperature. It should, however, be remembered that our object in the first instance was to prepare, not camphene, but acetate of borneol. On the other hand, I have not noticed any decomposition of the camphene under the circumstances of the reaction; and the crude substance, if not at once solidifiable, can readily be so obtained by conversion into the hydrochloride, which is easily purified and reconverted into camphene by means of aniline. The decomposition of turpentine hydrochloride is, according to my experience, not readily effected much below 250°. Wallach recommends the use of the hydrobromide, which would, however, be costly. It is not out of place here to recall the earlier literature on the preparation of camphene. Berthelot, in 1862 (*Compt. rend.*, **55**, 496), obtained camphene from both the hydrochloride and hydrobromide of turpentine by abstraction of the halogen acid in various ways. Riban, in 1875 (*Ann. Chim. Phys.* [5], **6**, 371), employed acetate of soda or potash for this purpose. Lauth and Oppenheim again, in 1867 (*Bull. Soc. Chem.*, **8**, 7), obtained camphene by heating its hydrochloride with aniline.

One other criticism of Wallach's remains to be noticed: as to our method of obtaining camphor from turpentine, he says that the conversion of turpentine into camphor has long since been realised in a manner which leaves nothing to be desired. This, however, is a matter of opinion.

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LXIII.—*Action of Nitrosyl Chloride on Metals.*

By J. J. Sudborough, B.Sc., A.I.C., Associate of Mason College, Birmingham.

Tilden, in his researches on nitrosyl chloride (Trans., 1874, **27**, 634), found that the chloride attacked the metals gold and platinum, forming definite crystalline compounds. The substances thus obtained were not analysed, and their true composition was therefore not known, although it was surmised that they were double chlorides, consisting of the metallic chloride combined with one or more molecules of nitrosyl chloride.

The following paper contains an account of experiments made with the object of studying the general behaviour of nitrosyl chloride towards the more common metals.

The nitrosyl chloride was prepared in the usual manner by the action of common salt on nitrosyl sulphate (Sudborough and Millar, Trans., 1891, **59**, 74).

The following metals were treated with the liquid chloride, either in the cold or on the water-bath:—

Magnesium, zinc, cadmium, lead, thallium, copper, silver, mercury, aluminium, iron, manganese, nickel, tin, antimony, bismuth, arsenic, gold, and platinum.

The method of procedure was as follows:—

About a gram of the pure metal, either in the form of a fine powder or as very thin foil cut into narrow strips, was placed in a stout tube, rounded off at one end. Both tube and metal were first thoroughly dried, an excess of nitrosyl chloride was condensed on the metal by placing the tube in a freezing mixture of salt and ice, and the upper end of the tube was then sealed off. In some cases the metal was attacked at once, even while in the freezing mixture. In such cases the tube was opened as soon as it was required, all excess of nitrosyl chloride was allowed to boil away (b. p. −8°), and the product left was transferred to a watch-glass and kept over sulphuric acid for an hour or so. A portion was then taken, and the percentage of metal in it determined. It was found almost useless to determine the chlorine, as the numbers for the different compounds vary so slightly. Thus, in the case of zinc—

$ZnCl_2$ requires..........	52·21	per cent.	of chlorine.
$ZnCl_2,NOCl$ requires	52·82	,,	,,
$ZnCl_2,2NOCl$ requires....	53·14	,,	,,

Hence in all cases the amount of metal found in the compound was used as a means of deciding its composition.

In those cases in which the metal was not attacked in the cold, the tube was slowly heated to 100° on the water-bath, and kept at that temperature for one, two, or three days. The tube was then allowed to cool, and the product treated as in the previous case.

Action on Magnesium.

The metal was not attacked by the liquid chloride in the cold, and even after heating on the water-bath for three days remained unaltered.

Action on Zinc.

This metal was rapidly attacked in the cold, with the evolution of copious nitrous fumes. On evaporating off the excess of nitrosyl chloride, a pale, lemon-yellow solid was left; this was very deliquescent, and readily dissolved in water with evolution of nitric oxide. On standing over sulphuric acid for two days, it turned white, and then dissolved in water without effervescence. A further quantity of the substance was therefore made, and analysed after it had been in the desiccator for about 15 minutes.

0·516 gram gave 0·2073 gram of ZnO.

	Theory for			
	$ZnCl_2$.	$ZnCl_2,NOCl$.	$ZnCl_2,2NOCl$.	Found.
Zn	47·8	32·22	24·3	32·20

A further determination of the zinc was made after the compound had stood for several hours over sulphuric acid.

0·4215 gram gave 0·1795 gram of ZnO.

	Found.
Zn	34·17

From these facts it appears that nitrosyl chloride readily acts upon zinc, forming a double chloride which has the composition $ZnCl_3,NOCl$, but this is somewhat unstable at ordinary temperatures and pressures.

Action on Cadmium.

No action occurred in the cold, and, therefore, the tube was heated at 100° for several days. At the end of the first day merely a white incrustation had been formed, but at the end of three days the whole of the metal had been acted upon. The product left after all the excess of nitrosyl chloride had boiled away was a pale-yellow compound which soon turned white; it dissolved in water without effervescence.

0·6791 gram gave 0·4745 gram of CdO.

	Theory for $CdCl_2$.	Found.
Cd	61·23	60·63

Action on Thallium.

The metal was not attacked in the cold, but was readily acted upon when heated at 100° for a few hours. Part of the product formed dissolved in the excess of nitrosyl chloride, and when this excess was allowed to boil away, a pale cream-coloured, crystalline compound was deposited. It was very deliquescent, and dissolved readily in water with brisk efforvescence. When gently heated, it melted, but on further heating decomposed.

The thallium was estimated by first reducing with sulphurous acid, and then oxidising with potassium permanganate.

1 c.c. of $KMnO_4$ = 0·0046056 gram of Fe.
„ = 0·0083704 „ Tl.

I. 0·5395 gram required 39·1 c.c. $KMnO_4$.
II. 0·5519 „ 39·6 „
III. 0·3901 „ 28·3 „
IV. 0·5260 „ 37·7 „

	Theory for		
	$TlCl_3$.	$TlCl_3,NOCl$.	$TlCl,TlCl_3,2NOCl$.
Tl........	65·74	54·28	60·52

	Found.			
	I.	II.	III.	IV.
Tl........	60·67	60·13	60·72	60·00

When thallium is burnt in chlorine, the compound $TlCl,TlCl_3$ is formed, and from the above analyses it appears that nitrosyl chloride attacks the metal, forming the compound $TlCl,TlCl_3,2NOCl$.

Action on Lead.

No action occurred in the cold, but after heating for six hours the lead had all been acted on. The resulting compound was a coarse white powder. It was not deliquescent, and was not decomposed by cold water, in which it was insoluble.

0·6766 gram gave 0·7400 gram $PbSO_4$.

	Theory for $PbCl_2$.	Found.
Pb	74·48	74·65

From this it appears that lead is only attacked by nitrosyl chloride when heated with it, and then merely forms the chloride $PbCl_2$.

Action on Copper.

As the copper was not attacked in the cold, the tube was heated at 100° for several days. In the first experiment made, only just sufficient nitrosyl chloride had been added to act upon all the copper. The result was a fine, black powder.

0·4825 gram gave 0·2336 gram CuO.

	Theory for.			
	$CuCl_2$.	$CuCl_2,NOCl$.	$Cu_2Cl_2,2NOCl$.	Found.
Cu	47·16	31·68	38·52	38·62

This black powder was readily decomposed by water, quantities of nitric oxide being evolved. When heated in an open tube to 100°, nitric oxide was given off, and anhydrous cupric chloride was left,

$$Cu_2Cl_2,2NOCl = 2NO + 2CuCl_2.$$

The compound is very deliquescent; in presence of moist air it turns first violet and then green. If left over sulphuric acid for several hours, it evolves nitric oxide, NO, which is absorbed by the acid, and leaves a residue of anhydrous cupric chloride.

A further quantity of copper was taken and treated with a large excess of liquid nitrosyl chloride, in order to see if any cupric compound could be obtained. After heating, however, for some time, the same black compound was formed.

0·4668 gram gave 0·2200 gram CuO.

	Theory for $Cu_2Cl_2,2NOCl$.	Found.
Cu	38·52	37·60

A further attempt was made to form a compound with cupric chloride by treating anhydrous cupric chloride with a quantity of the liquid. When, however, this was allowed to boil away, the cupric chloride was left in its original condition.

Thus the only compound formed by the action of nitrosyl chloride on copper is the unstable compound $Cu_2Cl_2,2NOCl$.

Action on Silver.

No action occurred in the cold, and on heating at 100° the metal became coated with a film of silver chloride, which prevented further action, and even after heating for three days this film was the only sign of any action which had taken place.

Action on Mercury.

This metal was attacked at once in the cold, and the product dissolved in the excess of nitrosyl chloride. After standing in the closed tube for a day, glistening crystals separated, and when the tube was placed in a freezing mixture, nearly the whole of the contents set into a glistening mass of golden plates. When, however, the tube was opened, all excess of nitrosyl chloride passed away, and there remained a white powder, which dissolved readily in cold water without effervescence. 1·000 gram gave 0·721 gram of Hg.

	Theory for		
	$HgCl_2$.	$HgCl_2,NOCl$.	Found.
Hg............	73·86	59·46	72·10

Thus it appears that mercuric chloride is the only compound produced by the action of nitrosyl chloride on mercury at ordinary temperatures.

Mercuric chloride itself was also treated with liquid nitrosyl chloride, but, on allowing the latter to boil away, the mercuric chloride was thrown down unchanged.

Action on Aluminium.

A brisk action took place in the cold, and copious nitrous fumes were evolved. The result of treating the metal with excess of nitrosyl chloride was a syrupy liquid, which on standing deposited a dull yellow solid. This dissolved in water, with evolution of much heat and slight effervescence.

I. 0·248 gram gave 0·0969 gram of Al_2O_3.
II. 0·9602 „ 0·3561 „ „

	Theory for		Found.	
	$AlCl_3$.	$AlCl_3,NOCl$.	I.	II.
Al........	20·29	13·61	20·67	19·65

Thus aluminium yields the simple chloride $AlCl_3$ when acted upon by nitrosyl chloride.

Action on Manganese.

Manganese was not acted upon at all in the cold, and even after heating at 100° for three days only a very small proportion of the metal was converted into the chloride.

Anhydrous manganese chloride was also treated with liquid nitrosyl chloride, but no action or combination of any kind took place.

Action on Iron.

This metal was acted upon immediately, and the product was a dull brownish liquid, which, on standing over sulphuric acid for some hours, set into a mass of minute, golden-brown crystals. These were very deliquescent when exposed to the air, but quite stable when kept over sulphuric acid. When gently heated, it volatilised, but, on further heating, decomposed, leaving a residue of ferric oxide. It dissolved readily in water, accompanied by evolution of much nitric oxide, NO.

I. 0·8295 gram gave 0·2973 gram of Fe_2O_3.
II. 0·3647 „ 0·1295 „ „

	Theory for $FeCl_3,NOCl$.	Found. I.	Found. II.
Fe..............	24·64	25·07	24·85

This same compound, $FeCl_3,NOCl$, had previously been obtained by passing nitrosyl chloride over anhydrous ferric chloride.

Action on Nickel.

No action occurred in the cold, and after heating at 100° for some days only a very small quantity of nickel chloride was formed, by far the greater part of the nickel being unattacked. The anhydrous chloride was also treated with nitrosyl chloride, but no double chloride could be isolated.

Action on Tin.

Metallic tin was immediately attacked, and the resulting product, after standing over sulphuric acid for several hours, was of a pale-yellow colour. It readily dissolved in water, and, on heating to a little above 100°, began to volatilise, and was deposited in the upper part of the tube in minute crystals. The sublimate thus formed dissolved in water with the evolution of nitric oxide.

I. 0·8288 gram gave 0·3152 gram of SnO_2.
II. 0·2410 „ 0 0930 „ „

	Theory for.		Found.	
	$SnCl_4,NOCl$.	$SnCl_4,2NOCl$.	I	II.
Sn	36·20	30·14	29·89	30·30

The compound $SnCl_4,2NOCl$ may also be obtained by treating stannic chloride with aqua regia (A. Baeyer, *Ber.*, 1874, 7, 1639). By this process it is obtained in large, yellowish crystals.

Action on Antimony.

Pure antimony was readily attacked in the cold, and the product formed dissolved in excess of nitrosyl chloride to a deep-red solution. On allowing the excess of nitrosyl chloride to escape, a minutely crystalline substance was deposited. This compound was of a canary-yellow colour. It was decomposed by water, with the evolution of nitric oxide, NO, and the precipitation of oxychloride of antimony. On heating, it melted, and then sublimed, being deposited as yellow needles.

I. 0·9305 gram gave 0·3784 gram SbO_4.
II. 0·7325 „ 0·2893 „

	Theory for		Found.	
	$SbCl_5,2NOCl$.	$(SbCl_5)_2,5NOCl$.	I.	II.
Sb	28·24	26·24	26·60	25·83

The compound would thus appear to have the composition

$$(SbCl_5)_2,5NOCl.$$

Antimony trichloride was also treated with liquid nitrosyl chloride, and the product obtained agreed in all its properties with that obtained from metallic antimony.

0·4377 gram gave 0·1756 gram SbO_4.

	Found.
Sb................	26·24

Thus the trichloride does not combine directly with nitrosyl chloride, but is first converted into the pentachloride, and this then forms the nitrosochloride, $(SbCl_5)_2,5NOCl$.

Action on Bismuth.

This metal was acted upon at once in the cold, and the product was an orange powder which dissolved in excess of nitrosyl chloride. It was very deliquescent, and was decomposed by treating with water.

I. 0·3458 gram gave 0·20685 gram of Bi_2O_3.
II. 0·42025 „ 0·2577 „

	Theory for.		Found.	
	$BiCl_3$.	$BiCl_3,NOCl$.	I.	II.
Bi........	66·25	54·85	53·64	54·98

Action on Arsenic.

This substance was readily attacked, forming a brown, oily liquid; on standing over sulphuric acid, it became colourless. It gave a white precipitate with water, but no effervescence occurred. The boiling point of the liquid was 132°, whereas arsenic trichloride boils at 134°.

0·738 gram gave 0·5035 gram As_2S_3.

	Theory for $AsCl_3$.	Found.
As	41·39	41·58

Thus arsenic is converted by the action of nitrosyl chloride into the trichloride, $AsCl_3$.

Action on Gold.

Pure gold was not attacked in the cold, but on heating at 100° for several days, an orange, crystalline powder separated out. This compound dissolved in water with evolution of nitric oxide, and, on strongly heating, decomposed, leaving a residue of metallic gold.

0·3540 gram gave 0·1885 gram Au.

	Theory for $AuCl_3,NOCl$.	Found.
Au	53·45	53·25

Action on Platinum.

This metal behaved in exactly the same manner as gold, the resulting product being a brownish-golden, crystalline substance. This dissolved in water, with evolution of nitric oxide, and, on strongly heating, decomposed, leaving a residue of metallic platinum.

0·457 gram gave 0·189 gram Pt.

	Theory for $PtCl_4,2NOCl$.	Found.
Pt	41·68	41·36

Weber (*Ann. Phys. Chem.* (*Pogg.*), **131**, 441) describes a golden, crystalline compound, obtained by treating platinum with *aqua regia* and evaporating. It is said to be very deliquescent and to dissolve in water with evolution of nitric oxide. The following are the results of his analyses :—

	Found.				Theory for $PtCl_4,2NOCl$.
	I	II	III.	IV.	
Pt	40·49	40·90	—	—	41·68
Cl	43·28	44·12	—	—	45·46
N	—	—	5·22	4·96	6·00

Based on these data he gave the compound the formula $PtCl_2,NO_3Cl,3OH$ (old notation). But there can be little doubt, both from his description and his analyses, that this compound is identical with that obtained by the action of nitrosyl chloride on platinum, and that it has the composition $PtCl_4,2NOCl$. Boyé and Rogers (*Phil. Mag.*, 1840, **17**, 397) also describe a compound obtained by heating platinum with *aqua regia;* this substance they regarded as a compound of platinum perchloride with nitric oxide. The following are the percentages they give :—

Pt	41·26	Cl	43·89

This is also the same compound, $PtCl_4,2NOCl$.

Summary.

The conclusions which may be drawn from the above experiments are summarised in the following statements :—

(1.) Magnesium is entirely unacted upon by liquid nitrosyl chloride both in the cold and at 100°. Manganese and nickel are only slightly attacked when heated with the liquid for several days at 100°.

(2.) Silver is slightly attacked, but further action is prevented by the formation of a film of silver chloride.

(3.) Cadmium, lead, thallium, copper, gold, and platinum are acted upon by the chloride when heated with it at 100° for several days.

(4.) Zinc, mercury, aluminium, iron, tin, antimony, bismuth, and arsenic are readily attacked even in the cold.

(5.) The following nitrosochlorides are capable of existing at ordinary temperatures:—

Formula.	Colour.	Properties.
$ZnCl_2,NOCl$	Lemon-yellow	Unstable.
$TlCl,TlCl_3,2NOCl$	Cream-yellow	Stable; decomposed on heating strongly
$Cu_2Cl_2,2NOCl$	Black	Unstable, evolving NO, and forming $CuCl_2$.
$FeCl_3,NOCl$	Golden-brown	Very stable, volatile at low temperatures.
$SnCl_4,2NOCl$	Dull yellow	Stable; volatilises and sublimes when heated.
$(SbCl_5)_2,5NOCl$	Lemon-yellow	Stable; sublimes when heated.
$BiCl_3,NOCl$	Orange-yellow	Unstable.
$AuCl_3,NOCl$	Deep orange	Stable; decomposes when very strongly heated.
$PtCl_4,2NOCl$	Golden-brown	Stable; decomposes when very strongly heated

All these nitrosochlorides are very deliquescent and are decomposed by water.

(6.) The following metals appear to be incapable of forming nitrosochlorides, which can exist at ordinary temperatures and pressures:—cadmium, lead, mercury, aluminium, manganese, nickel, and arsenic.

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LXIV.—*The Influence of Temperature on Germinating Barley.*

By T. Cuthbert Day.

It is a matter of common observation that, other conditions being the same, an increase of temperature within certain limits has a stimulating influence on germinating barley.

From a technical point of view, a study of the influence of temperature on germinating barley must be of great importance, seeing what a prominent part it plays in the proper growth of the corn on the malting floors.

It was with the intention of throwing some light, however small, on this still obscure subject that I have undertaken the present inquiry.

Experiments have been performed by several investigators as to the influence of temperature on the production of carbon dioxide by germinating seeds: by Sachs in 1865, Laskovsky in 1874, Borodin in 1875, Rischawi and A. Mayer in 1876, and R. Pedersen in 1880. The net result of the investigations is, that the production of carbon dioxide by germinating seeds increases with the temperature. The two last-named experimenters give curves illustrating the results of their experiments.

A knowledge of the amount of carbon dioxide exhaled by germinating barley during growth at various temperatures, as in the process of malting, is undoubtedly of great value, since a definite idea can then be formed of the amount of material decomposed, in order to furnish the gas. A good estimate of the germinative activity at different stages of growth may also be obtained by measuring the carbon dioxide produced at stated intervals. But, from a practical point of view, an insight into the constitution and properties of the malts produced by growing barleys at different temperatures would be of much greater value. Bearing these considerations in mind, I determined to grow identical samples of barley at different temperatures, after steeping them under precisely similar conditions to ensure identity in the amount of moisture absorbed. The growth was allowed to proceed at a uniform temperature, which was varied in the different experiments, for 10 days. The carbon dioxide produced was weighed from day to day, and at the end of the 10 days the germinated barley was dried at a low temperature, and securely sealed up for future analysis, with the object of gaining some knowledge of the constitution and properties of the different malts produced.

Method of Experiment.—The degree of germination and consequent internal change in the constituents of a barley corn is affected materially by four conditions, namely, moisture, temperature, aëration, and duration of growth. In order to study the effect of temperature, it was of course necessary to secure in the different experiments similarity as nearly as possible in the other conditions of growth. Since the success and trustworthiness of the experiments depend entirely on the method of conducting the germination from first to last, I shall devote some space to a full description of the processes and apparatus employed.

Fig. 1 is a sketch of the apparatus used for controlling the conditions of germination, and for collecting the carbon dioxide produced.

1. Four small bottles, the first three containing potash solution and the last one water, for purifying the air supplied to the germinating seed. The delivery tube into each bottle only just dips beneath the surface of the liquid.

2. A small flask containing a few c.c of distilled water, intended to saturate the air passing through it with moisture, at the same temperature as the germinating corn.

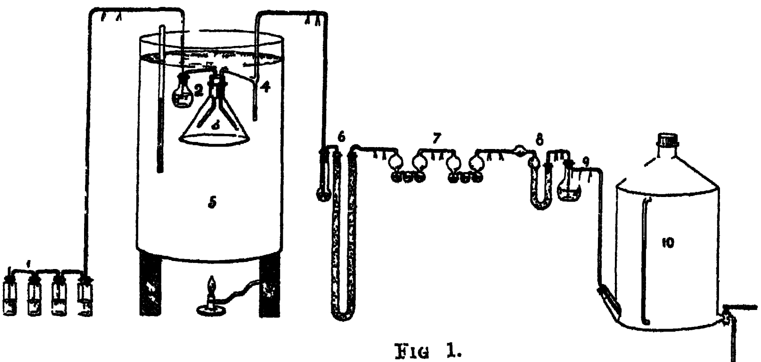

FIG 1.

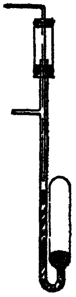

FIG. 2.

I have found by careful experiment that if barley be germinated in air exactly saturated with moisture, it will not absorb moisture from it even if the root appears to be in need of a further supply. Direct proof of this statement may be obtained by weighing the flask which supplies the moisture passing into the flask holding the germinating corn, and also the moisture passing out as collected in an absorption tube; in this determination of course the air must in the first place be dried. With a few slight variations, it will be found that the loss of weight by the moisture flask is exactly balanced by the gain of weight in the absorption tube.

The employment of air exactly saturated with moisture is absolutely essential to the success of the experiments, since, though it neither gives moisture to the growing seed nor takes any from it, the degree of moisture imparted to the seed in the first place, for the purpose of experiment, is preserved throughout the time required.

3. A conical shaped flask (700 c.c. capacity) to hold the corns experimented upon; it will accommodate about 45 grams of steeped barley lying in a layer one corn thick on the flat bottom. The flat bottom is employed to prevent any self heating of the corn and to secure uniformity in the temperature. The cork of the flask is well covered with tallow, which is found to effectually prevent the intrusion of moisture from without.

4. The exit tube from the germination flask. As it emerges from the flask it is bent downwards, and at the corner where it bends upwards a small descending tube is attached. This tube is designed as a trap to intercept any moisture condensing in the upper part of the exit tube, which might otherwise find its way into the germination flask, and thus vitiate the results. This is a most necessary contrivance.

5. A large galvanised iron vessel holding about 4 gallons, and filled with water, well under the surface of which the flasks 2 and 3 with their connecting tube are immersed. They are kept in place from above by a special holder not shown in the figure. The temperature of the water is kept constant by a delicate thermostat which regulates the size of the gas flame underneath. Over the gas flame is placed a piece of sheet iron to act as a disperser, and prevent unequal heating of the water vessel. During the course of an experiment, a large piece of flannel is thrown over the upper part of the vessel to prevent radiation and the consequent deposit of moisture on the sides of flask 3.

A separate sketch of the thermostat is given in Fig. 2. It differs from the ordinary mercurial thermostat in having the cylindrical bulb turned up. The upper part of the bulb, shown clear in the figure, is occupied by methylated alcohol (sp. gr. 0·825). The shaded portion of the bulb and tube is filled with mercury. Thermostats constructed on this principle are extremely delicate and reliable in their working. I had no difficulty in keeping a constant temperature for 10 days with this arrangement; in fact the temperature never varied more than 0·5° F. either way.

6. A small flask containing strong sulphuric acid and a long U-tube filled with pieces of pumice (previously ignited with sulphuric acid) saturated with strong sulphuric acid to completely dry the air coming from the germinating flask.

7. Two sets of potash bulbs containing strong potash solution to absorb the carbon dioxide exhaled during germination.

8. A U-tube containing pieces of pumice saturated with sulphuric acid to absorb the moisture carried over from the potash bulbs.

9. A small flask holding a little strong sulphuric acid, to act as a guard to 8.

10. The aspirator for drawing air through the whole apparatus, and regulated so as to draw about 7 to 8 litres in 24 hours. The long, hooked tube depending from the tap of the aspirator ensured a uniform rate of flow, which was usually about 16 drops per minute.

The efficiency of the apparatus was tested by weighing the absorption apparatus (7 and 8), connecting the different parts, and aspirating air for 24 hours. The gain of the weighed parts was found to be only 0·0018 gram.

The barley employed was a fine yellow Norfolk, harvested in 1885, and dried at 90° F. in January, 1886. The germinations were conducted from February to May (inclusive), 1886.

30 grams exactly of the dry barley (90° F.) were taken for each experiment. Each sample was carefully selected from the same bottle, and all doubtful corns, such as thin, broken, misshapen, or discoloured, were carefully picked out. The weighed samples were steeped in similar quantities of water for 60 hours at 60° F. in a water-bath kept at that temperature by means of a thermostat. The amount of water taken up by the corn in this way about corresponds to the quantity usually required in the malting process. The water was changed twice during the steep. The steep water and washings were collected, boiled down to rather under 100 c.c., made up to that volume exactly at 15·5° C., and the gravity taken. The amount of solids in solution was determined from the specific gravity by using the divisor 3·95, which, if not strictly accurate, is sufficiently near for the purpose.

At the end of the 60 hours' steep, the barley was drained and washed, and the adhering water removed by gentle pressure in a clean cloth. The steeped barley was then weighed. The increase of weight, including the weight of solids extracted during steep, gave the amount of water absorbed. The barley was then transferred to the germination flask. After weighing the absorption apparatus, the parts of the apparatus (Fig. 1) were connected together, all joints being securely tied, and air was continuously aspirated. At intervals of about 24 hours, the time being carefully noted, the absorption apparatus (7 and 8, Fig. 1) was again weighed, the increase in weight giving the quantity of carbon dioxide absorbed. The growth of the barley was continued for 10 days in each case, and the state of germination observed from day to day. Once in 24 hours the flask holding the corn was gently shaken to prevent matting together of the rootlets. At the end of 10 days, the germinated barley was extracted from the flask and weighed to prove that no moisture had been absorbed during the time of germination. It was found that the germinated barley lost a little in weight, the loss in every case being nearly represented by the weight of carbon oxidised to carbon dioxide. The actual loss sustained by the barley is really rather less than this, because rather more oxygen is absorbed than is required for the production of the carbon dioxide. The barley was then dried in an air-bath for two days at 120° F., separated from the rootlets, and both were then weighed. The malt was securely sealed up in a small bottle and reserved for analysis.

Six experiments were performed altogether, the germination being conducted at the following temperatures:—No. 1 at 38·3° to 43° F., No. 2 at 50° F., No. 3 at 55° F., No. 4 at 60° F., No. 5 at 65° F., and No. 6 at 70° F. These temperatures were maintained throughout the germinating period in each experiment. Experiment No. 1 should have been conducted at 40° F. exactly, but I had some difficulty in regulating the temperature at so low a point.

The Production of Carbon Dioxide.

Experiment 1.—30 grams of dry barley (90° F.) = 25·482 grams absolutely dry. Water absorbed during steep, 15·33 grams. Temperature during growth, 38·3° to 43° F.

Days.	Interval.	CO_2.	CO_2, mgrms. per hour.	State of germination.
	hrs.	grams.		
1	23½	0·0310	1·3	No signs of growth.
2	23¾	0·0237	1·0	Ditto.
3	22	0·0246	1·1	Just beginning to bud.
4	21½	0·0560	2·3	Buds considerably increased in size.
5	25¼	0·0591	2·3	In full bud, one corn showing a rootlet.
6	22¼	0·0495	2·2	Many corns breaking bud and showing a short single root.
7	25	0·0533	2·2	Most corns had a short single root rather longer than yesterday.
8	22¾	0·0597	2·6	Rootlets rather longer, some corns showing additional short rootlets.
9	21¼	0·0651	2·7	Rootlets a little increased in length.
10	24	0·0773	3·2	Rootlets rather increased in length, fresh and white.
Total...	237¼	0·5013		

Experiment 2.—30 grams of dry barley (90° F.) = 25·482 grams absolutely dry. Water absorbed during steep, 15·04 grams. Temperature during growth, 50° F.

Days.	Interval.	CO_2.	CO_2, mgrms per hour.	State of germination.
	hrs.	grams.		
1	23½	0·0432	1·8	Just commencing to bud.
2	24	0·0827	3·4	Full bud.
3	24¼	0·1286	5·3	Most corns with two or three short roots.
4	24	0·1436	6·0	Root considerably increased, white and strong.
5	21	0·1461	7·0	Growing steadily, spire beginning to show under husk.
6	25	0·1747	7·0	Root strong, increased in length.
7	24	0·1693	7·0	Growing steadily, spire about half up.
8	23¾	0 1640	6·9	Root increased in length, spire about half up.
9	24	0·1616	6·9	Root a good length, spire about half up.
10	24½	0·1511	6·2	Root fresh and strong, about equal in length to an ordinary 7 or 8 day couch; spire about half up.
Total...	238	1·3682		

Experiment 3.—30 grams of dry barley (90° F.) = 25·482 grams absolutely dry. Water absorbed during steep, 15·35 grams. Temperature during growth, 55° F.

Days.	Interval.	CO_2.	CO_2, mgrms. per hour.	State of germination.
	hrs.	grams.		
1	19	0·0515	2·7	Just budding.
2	24	0·1257	5·2	Most corns showing a short root.
3	26½	0·2132	8·0	Root much increased.
4	23¼	0·2075	8 9	Root considerably increased, spire showing under husk.
5	22	0·2040	9·3	A long, white root, spire nearly half up.
6	25	0 2306	9·2	Root increased in length, spire nearly half up.
7	23¾	0·2274	9·6	A long, fresh root, spire half up.
8	25¼	0·2341	9·3	Root still increasing, spire a little more than half up
9	22½	0·1930	8 6	Root still strong and fresh, spire half to two-thirds up.
10	24¼	0·2020	8·3	Root long and fading slightly, spire half to fully up.
Total...	235½	1·8890		

Experiment 4.—30 grams. of dry barley (90° F.) = 25·482 grams absolutely dry. Water absorbed during steep, 14·98 grams. Temperature during growth, 60° F.

Days.	Interval.	CO_2.	CO_2, mgrms. per hour.	State of germination.
	hrs.	grams.		
1	23¼	0·0897	3·9	Nearly full bud.
2	21¾	0·1975	9·1	Beginning to make root.
3	25½	0·2619	10·3	Root increasing rapidly.
4	25	0·2794	11·2	Root growing rapidly, spire about one-third up.
5	23¾	0·2436	10·3	Strong white root, growing fast; spire half up.
6	21¼	0·2170	10·0	Root healthy and growing, spire one-third to two-thirds up.
7	26	0·2299	8·8	A long, healthy root, spire one-third to nearly up.
8	23½	0·1894	8·1	Root still healthy, spire half to full up.
9	24	0·1785	7·4	Root beginning to fade a little, spire half to full up.
10	24¼	0·1748	7·2	Root long and slightly faded, spire half to full up. One corn with a little blue mould.
Total...	238¼	2·0617		

Experiment 5.—30 grams of dry barley (90° F.) = 25·482 grams absolutely dry. Water absorbed during steep, 15·00 grams. Temperature during growth, 65° F.

Days.	Interval.	CO_2.	CO_2, mgrms. per hour.	State of germination.
	hrs.	grams.		
1	23	0·1397	6·1	Breaking bud and showing a single root.
2	21¾	0·2682	12·3	Very rapid growth of root. Many corns with two or three long roots.
3	24½	0·3135	12·8	Root still growing rapidly.
4	25	0·3164	12·7	Root considerably increased, spire about half up.
5	23½	0·2548	10·8	A long, curly, healthy root, spire half up.
6	23½	0·2329	9·9	Root still growing and healthy, spire rather more than half up.
7	23¾	0·2136	9·0	Root still healthy, but slightly faded, spire about two-thirds up.
8	26¼	0·2025	7·7	Root very long and still healthy, but a little faded; spire half to three-quarters up.
9	21¾	0·1885	8·7	Root a little more faded.
10	27¼	0·1774	6·5	A long root, still healthy, but a little faded; spire half to fully up.
Total...	240¼	2·3075		

Experiment 6.—30 grams of dry barley (90° F.) = 25·482 grams absolutely dry. Water absorbed during steep, 15·38 grams. Temperature during growth, 70° F.

Days.	Interval.	CO_2.	CO_2, mgrms. per hour.	State of germination.
	hrs.	grams.		
1	22¼	0·1541	6·9	A short root on most of the corns.
2	23¼	0·3262	11·0	Most corns with several short roots.
3	23	0·3333	14·5	Quite a bushy root, strong and fresh looking; spire one-third up.
4	24¼	0·2959	12·1	A long, curly root, spire about half up.
5	22½	0·2531	11·2	Root strong and vigorous, spire half up.
6	23½	0·2344	10·0	A good root, spire half to two-thirds up.
7	26	0·2403	9·2	Root rather longer and still fresh, spire about two-thirds up.
8	23¼	0·2140	9·2	Root long, still healthy; spire half to fully up.
9	25½	0·2146	8·4	Root still fairly fresh, spire half to fully up.
10	24¼	0·2181	9·0	Root a little faded, spire half to fully up.
Total...	238¼	2·4840		

The figures given in the foregoing experiments show plainly the effect of temperature on the production of carbon dioxide by germinating barley. The most striking feature is the rapid increase in the evolution of the gas during the first few days of growth, as shown by the amount produced per hour each day, especially at the higher temperatures. As the temperature is raised, the maximum evolution takes place at an earlier stage of germination.

I give three series of curves, at the end of the paper, the first showing the progress of the evolution of carbon dioxide from day to day from start to finish in each experiment; the second series, the evolution in milligrams per hour each day for each experiment; and the third series consisting of two curves combining the six experiments, and showing the total production of carbon dioxide and of dry root at the different temperatures. An inspection of these curves will show more plainly the effect of temperature during germination than any number of figures, however carefully arranged.

To begin with Series I, it will be noticed that, as the temperature is raised, the curves tend to lie closer together, showing pretty clearly that, as the temperature rises, the corresponding increase in the production of carbon dioxide tends to diminish. The next point to be observed is the character of the curves themselves. The three lowest curves have their convexity, generally speaking, turned

CUTHBERT DAY

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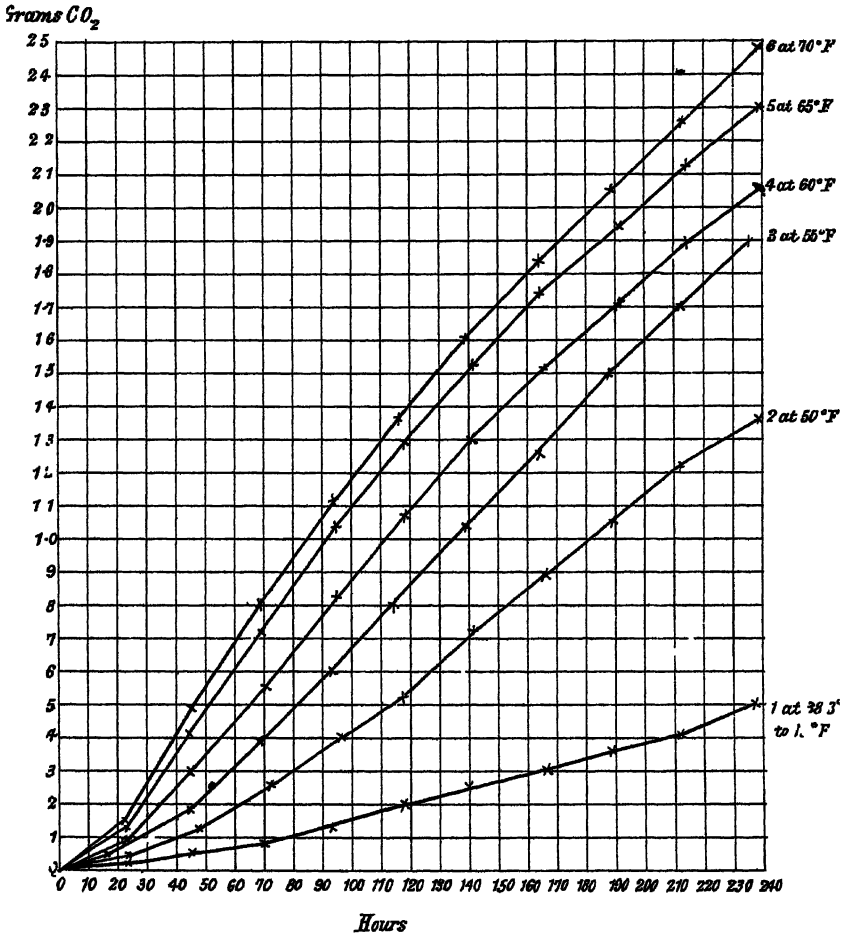
SERIES I.

CURVES SHOWING THE PRODUCTION OF CARBON DIOXIDE, IN GRAMS, BY GERMINATING BARLEY AT DIFFERENT TEMPERATURES THE NUMBERS OPPOSITE THE CURVES REFER TO THE EXPERIMENTS FROM WHICH THEY WERE OBTAINED

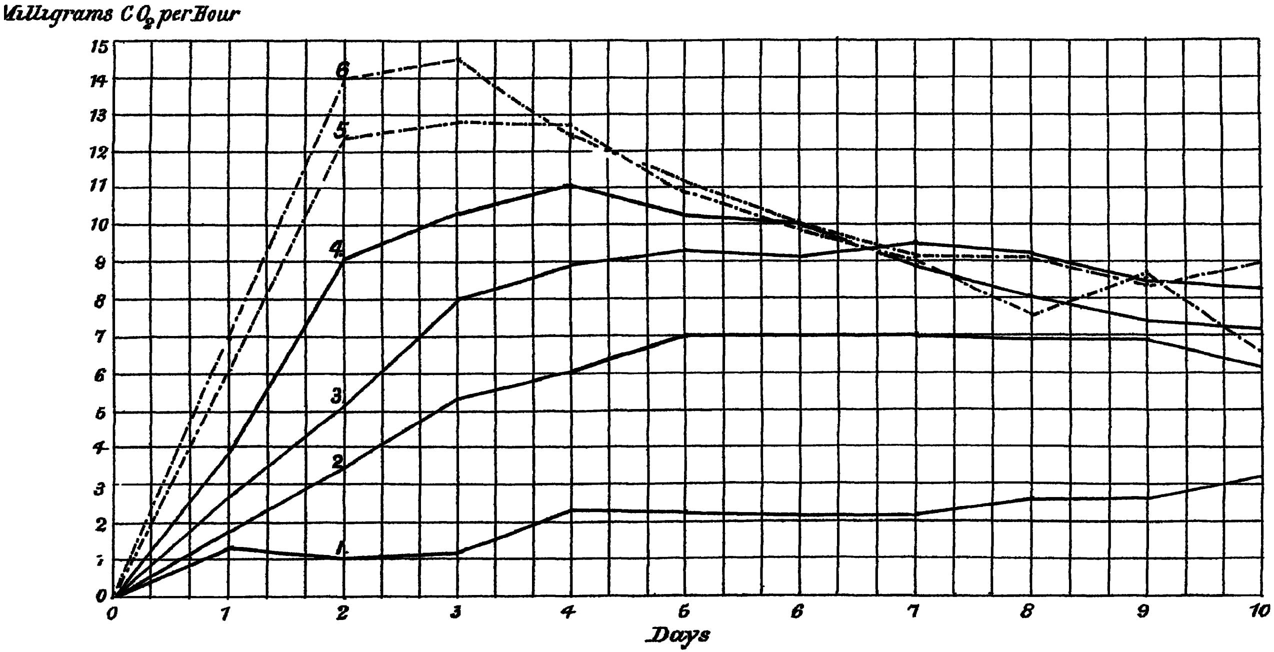


Journ Chem Soc Sept 1891

SERIES II

CURVES SHOWING THE PRODUCTION OF CARBON DIOXIDE IN MILLIGRAMMES PER HOUR FROM DAY TO DAY, BY GERMINATING BARLEY, AT DIFFERENT TEMPERATURES.

THE EXPERIMENTS TO WHICH THE CURVES REFER ARE DENOTED BY THE NUMBER ON EACH CURVE



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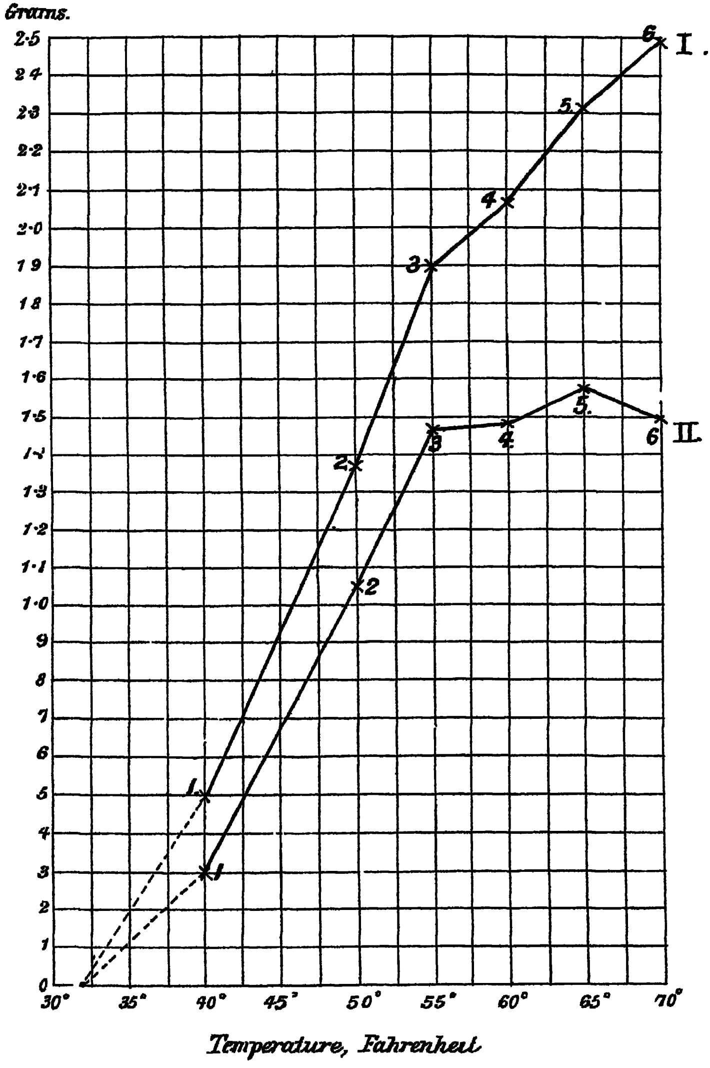
SERIES III.

CURVES SHOWING THE PRODUCTION OF CARBON DIOXIDE AND DRY ROOT
AT DIFFERENT TEMPERATURES IN ALL SIX EXPERIMENTS.

CURVE I. RELATES TO WEIGHT OF CARBON DIOXIDE IN GRAMS

CURVE II. RELATES TO WEIGHT OF DRY ROOT IN GRAMS

THE FIGURES ON THE CURVES REFER TO THE DIFFERENT EXPERIMENTS



towards the horizontal line, while the three highest curves have their convexity turned in the opposite direction.

The curves given in Series II show, in a remarkable way, the rate of production of carbon dioxide for each day as measured in milligrams per hour. In Experiment 1, at 40° F., allowing for the small variations of temperature in this case, the rate of production of dioxide gradually increases from start to finish. In Experiments 2 and 3, at 50° and 55° F. respectively, the evolution of the gas increases till the fifth day of growth, after which, practically speaking, it remains on a dead level, though a slight falling off is noticed towards the end. The curve for Experiment 4 shows the greatest production of carbon dioxide on the fourth day, after which period the rate of evolution steadily diminishes. In Experiments 5 and 6, at 65° and 70° F., the evolution of the gas, though very rapid at first, reaches its highest point rather earlier; for No. 5, between the third and fourth days, and for No. 6 on the third day of growth. In both these experiments, the rate of decrease from the maximum is seen to be pretty rapid to the close.

An inspection of the curves given in Series III, comparing the total quantity of carbon dioxide produced in the six experiments with the weight of dry root formed, shows some degree of similarity in their form. Each bend of the one has a counterpart in the other. The chief point to be noticed, however, is that, though there is a considerable falling off in the increase of the quantity of carbon dioxide produced when the temperature rises above 55° F., yet the effect of the increase of temperature above the same point in diminishing the increase in the weight of dry root formed is very much more marked, as the curve plainly shows by the sudden bend at this point towards the horizontal. I shall refer more particularly to this peculiarity in these two curves when I come to consider the constitution of the different malts.

I will now give the results of the experiments as they relate to the weight of malt and root obtained, the carbon oxidised, and the loss during steep, &c.

It will be seen from the figures in the following table that the amount of malt obtained decreases as the temperature is raised, up to 65° F., a slight increase being shown at 70° F. over the quantity at 65° F.

The amount of root increases up to 65°, and at 70° F. a slight decrease is observed.

The quantity of carbon oxidised increases with the temperature all through the series.

The six malts obtained were carefully analysed by methods or modifications of methods chiefly due to Mr. C. O'Sullivan, and published in the Transactions of the Chemical Society.

Experiment ..... Temperature	1. 38·3° to 43° F.	2. 50° F.	3. 55° F.	4. 60° F.	5. 65° F.	6. 70° F.
	grams	grams.	grams	grams	grams.	grams.
Absolutely dry malt	21·195	23·258	22·553	22·435	22·171	22·194
" " root	0·298	1·048	1·461	1·483	1·578	1·487
Carbon oxidised....	0·1458	0·3731	0·5152	0·5623	0·6293	0·6775
Loss in steep	0·220	0·280	0·272	0·252	0·190	0·240
Sum..............	25·1588	24·9591	24·8012	24·7323	24·5683	24·5985
Absolutely dry barley............	25·4820	25·4820	25·4820	25·4820	25·4820	25·4820
Loss, mostly due to water liberated by probable combustion of carbohydrates	0·3232	0·5229	0·6808	0·7497	0·9137	0·8835

The following determinations were made and calculated to the dry malt; and from the numbers thus obtained, the results were calculated to the corresponding quantity of dry barley:—

1. Fatty matter.
2. Mixed sugars.
3. Soluble carbohydrates other than sugars. Bodies belonging probably to the class of amylans.
4. Starch.
5. Cellulose.
6. Nitrogenous substances soluble in water at 40° C., and permanently soluble after boiling.
7. Nitrogenous substances soluble in water at 40° C., and coagulated on boiling.
8. Solids permanently soluble in water at 40° C.
9. Starch conversion products formed by the action of diastase at 40° C.

The numbers obtained under 9 are intended to convey some notion of the diastatic activity of the different malts. The amount of the starch conversion products due to the action of the diastase in the malt on its own starch at a low temperature (40° C.) is found by deducting the sum of the percentages of sugars, of soluble carbohydrates other than sugars, and of the permanently soluble nitrogenous compounds from the percentage of solids dissolved by water at 40° C., as found under 8.

These figures show either that the malts possess different diastatic powers, or that the starches present in the malts are in such a condition as to render them susceptible to the action of diastase in very different degrees. For my own part, I am inclined to favour the first supposition, namely, that the amount of starch conversion products found was due to the activity of the diastatic ferment in each case.

I append here the figures obtained in the analyses of the six samples of malt produced in the experiments (p. 676).

An examination of the figures relating to the composition of the dry malt reveals a decided difference in their character throughout the series. Taking the different constituents determined in the order they are set down, the fats appear to decrease in quantity, gradually, as the temperature of germination is raised. The sugars increase (with a jump in the first 10 degrees) up to 55° F., after which the amount found is less, though slightly higher at 70° F. than at 65° F.

The soluble carbohydrates other than sugars increase, as in the case of the sugars, very rapidly at first; at 50°, 55°, and 60° F. they remain practically unaltered; but at 65° and 70° F. they show a falling off in quantity. The starch decreases rapidly between 40° and 50° F., and at 55° F. still shows a decided decrease. The figures show an increase from this point up to 70° F. The quantity of cellulose tends to decrease as the temperature rises. The permanently soluble nitrogenous compounds show an increase up to 55° F., but beyond this point up to 70° F. there is a gradual decrease. The coagulable nitrogenous compounds are present in small quantity; there is a gradual increase up to 60° F., above which temperature rather less is found. The starch conversion products formed by digesting the malts with water at 40° C. follow the same rule as the permanently soluble nitrogenous bodies, showing a maximum at 55° F.

The most important point brought to light by a consideration of these results is, that the sugars reach their maximum, the starch suffers the greatest amount of degradation, the permanently soluble nitrogenous compounds are present in greatest quantity, and the diastatic ferment is the most active, all in the malt grown throughout at a temperature of 55° F. The evidence as to the peculiar change in the composition of the malts which were grown at a temperature above 55° F. is strongly corroborated by the determination of the carbon dioxide and dry root formed. A mere inspection of the two curves in Series III demonstrates clearly enough that there must be some remarkable change at the above-mentioned point. It appears, also, as if, at the higher temperatures, a portion at least of the carbon dioxide was produced more at the expense of the sugars and other soluble carbohydrates, formed at the earlier stages of germination, than that the starch alone, by its oxidation, furnished the whole of the gas.

I.—Calculated on the Dry Malt.

No. of experiment.		Fatty matter.	Sugars.	Soluble carbohydrates other than sugars.	Starch.	Cellulose.	Nitrogenous bodies soluble at 40° C., and permanently soluble after boiling. N × 6·33.	Nitrogenous bodies soluble at 40° C. coagulated on boiling.	Solids permanently soluble at 40° C.	Starch conversion products formed by action of diastase at 40° C.	Dry malt.	Dry barley; proportion to dry malt.
		p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c		
40° F.	1	2·11	2·86	5·03	60·14	8·08	2·70	0·31	16·28	5·69	100	104·03
50	2	1·95	7·17	8·11	54·45	7·23	4·18	0·43	33·37	13·96	100	109·56
55	3	1·92	8·29	8·05	53·12	7·56	4·19	0·45	36·38	15·85	100	112·54
60	4	1·83	6·40	8·24	55·28	7·43	3·80	0·51	29·97	11·53	100	113·49
65	5	1·72	5·59	7·25	56·04	7·33	3·49	0·50	27·08	10·75	100	114·93
70	6	1·72	5·85	7·23	56·26	7·15	3·29	0·48	24·96	8·59	100	114·81

II.—Calculated on the Dry Barley.

											Carbon oxidised.	Carbon oxidised reckoned as $C_6H_{10}O_5$.
		p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
	1	2·03	2·75	4·84	57·81	7·77	2·59	0·30	15·65	5·47	0·57	1·28
	2	1·78	6·54	7·40	49·70	6·60	3·77	0·39	30·46	12·74	1·46	3·28
	3	1·71	7·37	7·15	47·20	6·72	3·72	0·40	32·33	14·08	2·02	4·54
	4	1·61	5·64	7·26	48·71	6·55	3·35	0·45	26·41	10·16	2·21	4·97
	5	1·50	4·86	6·31	48·76	6·38	3·04	0·44	23·56	9·35	2·47	5·56
	6	1·50	5·10	6·30	49·00	6·23	2·87	0·42	21·74	7·48	2·66	5·98

The numbers showing the composition of the malts as calculated to dry barley (II) from the proportions given in the first table (p. 674) are chiefly useful in furnishing a test as to the general accuracy of the determinations.

If we add together the numbers representing the sugars, soluble carbohydrates other than sugars, starch cellulose, and carbon oxidised reckoned as $C_6H_{10}O_5$, we ought to obtain numbers showing a small decrease from 40° F. up to 55° F. sufficient to allow for the carbohydrates formed in the rootlet; but above 55° F the numbers should be nearly the same, though least at 65° F., where the maximum amount of root was obtained.

An application of this test gave the following results :—

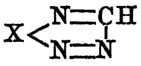
Temperature ...... Experiment	40° F 1.	50° F 2.	55° F. 3.	60° F. 4.	65° F 5.	70° F. 6
Sugars	2·75	6·54	7·37	5·64	4·86	5·10
Soluble carbohydrates ..	4·84	7·10	7·15	7·26	6·31	6·30
Starch................	57·81	49·70	47·20	48·71	48·76	49·00
Cellulose	7·77	6·60	6·72	6·55	6·38	6·23
Carbon as $C_6H_{10}O_5$	1·28	3·28	4·54	4·97	5·57	5·98
Totals	74·45	73·52	72·98	73·13	71·88	72·61

These totals turn out nearly as expected, though No. 5 appears to be rather too low as compared with the others. On the whole, considering the nature of the analyses and the probable individual differences in the samples of barley grown, the result may be considered as highly satisfactory, and as affording fairly reliable testimony to the value of the experiments. Of course, the totals above given are partly derived on the assumption that the whole of the carbon dioxide formed during germination is derived from the oxidation of a carbohydrate of the empirical formula $C_6H_{10}O_5$; whereas I am inclined to infer, from a consideration of the analytical results, that a small part of this gas, especially at the higher temperatures, is probably derived from the nitrogenous compounds, both soluble and insoluble, present in the barley.

LXV.—*Researches in the Triazine Series.*

By Raphael Meldola, F.R.S., and Martin O. Forster.

According to the nomenclature proposed by Widman (*Journ. f. prakt. Chem.*, 1888, **28**, 192), the closed chain compounds containing 3 atoms of nitrogen and 1 atom of carbon of the form



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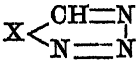
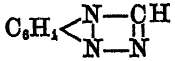
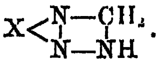


are termed respectively *α*- and *β*-triazines. In 1889, *α*-phentriazine and some of its derivatives were obtained by Bischler (*Ber.*, 1889, **22**, 2801) and by Bischler and Brodsky (*ibid.*, 2809), but these authors give a different grouping to the nitrogen atoms:—

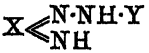


Some members of the *α*-series were prepared simultaneously last year, by Goldschmidt and Rosell (*Ber.*, 1890, **23**, 505), from orthoamidoazo-compounds and benzaldehyde, and by one of the authors by this method, as well as by inner condensation from orthoazo-derivatives of benzylidene-*β*-naphthylamine (Trans., 1890, **57**, 328). More recently Goldschmidt and Poltzer have prepared many other triazines by the action of various aldehydes on orthoamidoazo-compounds (*Ber.*, 1891, **24**, 1000).

The triazines thus prepared are derivatives of a dihydrotriazine of the type

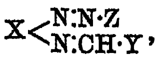


Goldschmidt and Poltzer consider that the formation of a triazine by the action of an aldehyde on an orthoamidoazo-compound is an argument in favour of the hydrazono formula of the latter,



$$X{<}^{N\cdot NH\cdot Y}_{NH}$$

(*Ber.*, 1891, **24**, 1002). On the other hand, it has been recently pointed out by one of us and F. Hughes (this vol., p. 381) that the triazines are capable of being formed from benzylidene orthoazo-compounds of the form



$$X{<}^{N{:}N\cdot Z}_{N{:}CH\cdot Y},$$

which cannot be represented as hydrazones. The triazines are produced from these compounds by the simple rearrangement of the bonds. This rearragement takes place readily under the influence of acids, as pointed out by one of us last year, and we have availed ourselves of this discovery for the preparation of a number of substituted triazines by a method which has been found so generally applicable that one description will suffice.

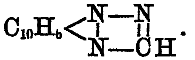
Preparation of Substituted Triazines.

The azo-derivative of β-naphthylamine (or other orthoamidoazo-compound) is introduced into a dry flask, and covered with from 10 to 20 times its weight of glacial acetic acid according to its degree of solubility. The calculated quantity of benzaldehyde or other aldehyde is then added, and the contents of the flask kept gently boiling for about an hour. The solution is at first of a deep-orange or orange-red colour, but, as the triazine is formed, the colour becomes lighter, and an almost colourless solution is finally obtained if the operation has been successfully conducted. When cold, the contents of the flask are poured into a large volume of cold water. In most cases, the triazine separates out as a granular, whitish precipitate, which can be collected and washed. In the case of triazines containing but few acid radicles, and therefore possessing a somewhat basic character, it may be necessary to neutralise the excess of acetic acid by an alkali to ensure the complete precipitation of the triazine. If an excess of aldehyde is used, as is necessary if the original acetic acid solution has been made too weak, the separation of the triazine does not take place so readily, and the solution, after being poured into water, must be boiled for some time to expel the excess of aldehyde. It is only after this condition has been complied with that the triazine can be obtained, under such circumstances, in a condition fit for filtration. The method described is applicable to all orthoamidoazo-compounds, and offers the advantage of enabling the triazines to be prepared with practically theoretical yields, under ordinary pressure, without employing very high temperatures, and with only the theoretical quantity of the aldehyde.

Nomenclature of Triazine Derivatives.

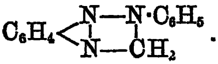
The simplest triazine of the aromatic series is the phentriazine of Bischler. The corresponding compounds of the naphthalene series may be termed naphtriazines, or, more euphoniously, naphthotriazines. The derivatives dealt with in the present paper are substituted α-dihydronaphthotriazines. For the sake of brevity, the prefix

" α-dihydro- " will be omitted. The parent compound of the present series is naphthotriazine,

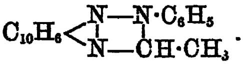


$$C_{10}H_6<\begin{array}{l}N—N\\ |\quad\;\; \|\\ N—CH\end{array}.$$

The triazines described in the present paper contain two or three aromatic nuclei, in any or all of which substituents may be present. It has therefore been found convenient to adopt some system of nomenclature by which the position of the substituents may be indicated. All triazines may be regarded as resulting from the union of an azo-group, $X\cdot N{:}N\cdot$, with an aldehyde residue, $Y\cdot CH{:}$. The radicles X and Y may have therefore the abbreviated prefixes *az* and *ald* attached to them respectively. The naphthylene (or phenylene) nucleus requires no prefix, as its name is expressed in the name of the triazine. The following examples will illustrate the application of the proposed system of nomenclature :—

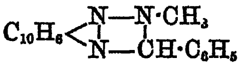


$$C_6H_4<\begin{array}{l}N—N\cdot C_6H_5\\ |\quad\;\; |\\ N—CH_2\end{array}.$$ *az*-Phenylphentriazine.*

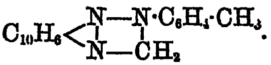


$$C_{10}H_6<\begin{array}{l}N—N\cdot C_6H_5\\ |\quad\;\; |\\ N—CH\cdot CH_3\end{array}.$$ *az*-Phenyl-*ald*-methylnaphthotriazine.

The last compound has been prepared by Goldschmidt and Poltzer (*Ber.*, 1891, **24**, 1004) by the action of acetaldehyde on benzeneazo-β-naphthylamine. According to the nomenclature of these authors, the compound is termed " methylphenyldihydro-β-naphthotriazin," but this term is equally applicable to compounds of the formulæ

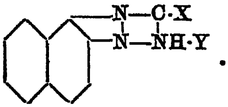


$$C_{10}H_6<\begin{array}{l}N—N\cdot CH_3\\ |\quad\;\; |\\ N—CH\cdot C_6H_5\end{array}$$ and



$$C_{10}H_6<\begin{array}{l}N—N\cdot C_6H_4\cdot CH_3\\ |\quad\;\; |\\ N—CH_2\end{array}.$$

The system of nomenclature which is here proposed, although, perhaps, somewhat more cumbrous, avoids all ambiguity. It is unnecessary to multiply illustrations of the application of this method, as other examples will be furnished by the compounds described subsequently. It will be understood that the naphthotriazines hitherto prepared have the substituents in the α-β-ortho-positions,



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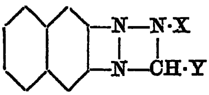
* Might be prepared by the action of formaldehyde on *o*-amidoazobenzene.

Isomeric forms are possible, viz. :—



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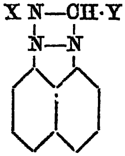

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but the triazines of these types have not yet been prepared.

Diphenylnaphthotriazine and Derivatives.

The above compound is very readily prepared in the manner described; its properties have already been made known in previous communications (*Ber.*, 1890, **23**, 506). This triazine was selected with the object of ascertaining, in the first place, whether substitution took place in any definite manner, or whether a mixture of derivatives resulted from the action of the ordinary substituting agents, such as bromine, nitric acid, and sulphuric acid.

Action of Bromine.—On adding bromine, dissolved in glacial acetic acid, to a solution of the triazine in the same solvent as long as a precipitate is formed, there is obtained a whitish substance which, after being collected and washed, was crystallised from alcohol and then several times from toluene till the melting point was constant. The product thus obtained forms flat, ochreous needles melting at 214°. Analysis showed that this compound, although apparently definite, was a mixture of the di- and tri-bromo-derivatives, and these could not be separated by further crystallisation. The results of analysis, after four successive crystallisations, were :—

I.	0·2020	gram gave	0·1610	gram AgBr	= 33·91	per cent. Br.
II.	0·1861	,,	0·1537	,,	= 35·14	,,
III.	0·1794	,,	0·1491	,,	= 35·36	,,
IV.	0·1352	,,	0·1133	,,	= 35·65	,,

Calculated for $C_{23}H_{15}Br_2N_3$, 32·45 per cent. Br.
,, $C_{23}H_{14}Br_3N_3$, 41·95 ,,

Action of Nitric Acid.—The triazine was added in small portions to about 10 times its weight of well-cooled fuming nitric acid (1·5 sp. gr.). The substance dissolves quietly without much development of heat. After being allowed to stand in the cold for about an hour, the nitric acid solution was poured into cold water, and the ochreous precipitate thus thrown out was collected, washed with cold water, and dried. The dry product was very insoluble in most solvents, and could only be purified by dissolving in nitrobenzene and precipitating with alcohol. In this way three crops of minute, ochreous crystals were obtained by successive filtrations and precipitations:—

First Crop.—This was filtered off as soon as formed, washed with alcohol, and dried. The melting point was vague (275—290°), so the dry product was redissolved in nitrobenzene, and again precipitated by alcohol. After being washed with alcohol and dried, the melting point was above 300° (about 305°), and the analytical results indicated a tetranitro-derivative:—

0·1300 gram gave 20·7 c.c. moist N at 8° C. and 758 mm. bar.

	Calculated for $C_{23}H_{13}(NO_2)_4N_3$	Found.
N	19·02 per cent.	19·15 per cent.

Second Crop.—This consisted of minute, ochreous scales melting at 205°.

0·1042 gram gave 15·3 c.c. moist N at 72° C. and 752·8 mm. bar.

	Calculated for $C_{23}H_{14}(NO_2)_3N_3$.	Found.
N	17·87 per cent.	17·60 per cent.

Third Crop.—This only separated after long standing, and was treated in the same way as the other crops. After being purified by dissolving in nitrobenzene and precipitating by alcohol, the product had a melting point of 249°:—

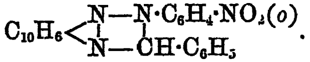
0·1041 gram gave 15·7 c.c. moist N at 11·5° C. and 760·4 mm. bar.

	Calculated for $C_{23}H_{14}(NO_2)_3N_3$.	Found.
N	17·87 per cent.	17·93 per cent.

This also agrees with the formula of a trinitro-derivative. It appears, therefore, that fuming nitric acid in the cold gives rise to a mixture of tetranitro- and two isomeric trinitro-triazines. As practically nothing is known as yet concerning the way in which substitution takes place in the triazines, it appeared that the products obtained by the action of bromine and nitric acid were too complex and too difficult to separate to enable this part of the subject to be profitably pursued until a series of standard synthetically-prepared triazines, with the substituents in known positions, had been studied. The experiments were accordingly carried on in this direction, and the results obtained form the subject of the present communication.

We may add that the triazine, when heated with about 10 times its weight of strong sulphuric acid at 100° for 10 minutes, is converted into a sulphonic acid which is extremely soluble in water, and of which the barium and potassium salts are uncrystallisable. As the monosulphonic acid, prepared synthetically, is quite insoluble in water, there is no doubt that the product thus obtained is a polysulphonic acid.

Az-o-NITROPHENYL-*ald*-PHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{matrix}N-N\cdot C_6H_4\cdot NO_2(o)\\ | \quad\quad |\\ N-CH\cdot C_6H_5\end{matrix}.$$

Orthonitrobenzeneazo-β-naphthylamine (this vol., p. 373) was boiled with about ten times its weight of glacial acetic acid and the theoretical quantity of benzaldehyde for an hour. The product, after being precipitated by water, washed, and dried, was twice crystallised from boiling alcohol. It separates slowly from the solution in the form of dense, semi-transparent, light ochreous, prismatic needles, mixed with a small quantity of some modification consisting of small, opaque, yellowish needles collected into warty agglomerations. The latter were present in very small quantity, as compared with the main product, and we were at first disposed to believe that some impurity was present in the original compound, and had become segregated by crystallisation. Further experience with the nitrotriazines, and the analysis of the two forms, has shown, however, that these compounds are susceptible of very remarkable modification in crystalline form, due possibly to some kind of isomerism (physical or stereochemical ?). The melting points were :—

Ochreous prisms	210—211°.
Opaque needles............	208—209°.

The two forms were so distinct that they could be easily separated for analysis :—

I. 0·2382 gram (prisms) gave 0·6324 gram CO_2 and 0·0916 gram H_2O.

II. 0·2055 gram (prisms) gave 0·5481 gram CO_2 and 0·0878 gram H_2O.

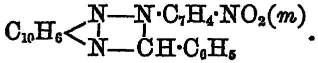
III. 0·1529 gram (prisms) gave 19·1 c.c. moist N at 11° C. and 750·2 mm. bar.

IV. 0·0790 gram (needles) gave 9·8 c.c. moist N at 12° C. and 757·2 mm. bar.

	Calculated for $C_{23}H_{16}N_4O_2$.	Found. I.	II.	III.	IV.
C	72·63	72·40	72·75	—	—
H	4·21	4·27	4·74	—	—
N	14·73	—	—	14·68	14·65

The quantity of the opaque form was too small for further analysis. The transformation of the transparent into the opaque form is apparently brought about by heat, as on heating in a dry tube the transparent prisms become opaque at about 145°.

Az-m-NITROPHENYL-*ald*-PHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{matrix}N—N{\cdot}C_7H_4{\cdot}NO_2(m)\\ |\quad\quad |\\ N—CH{\cdot}C_6H_5\end{matrix}.$$

This compound was prepared in the same manner as the preceding, rom metanitrobenzeneazo-β-naphthylamine (Trans., 1884, **45**, 116) nd benzaldehyde. It dissolves in boiling alcohol very slowly, and we have since found that this property is generally characteristic of the nitrotriazines, those compounds all dissolving with extreme slowness, and separating with equal slowness from their solutions. Until this property had been realised, we attributed slowness of solution to actual insolubility, and our first preparations were accordingly crystallised from fusel oil, in which the substance dissolves more readily at the boiling point of the solvent. The compound was obtained by this means in the form of a dense cake of ochreous, rhombic crystals melting, after washing with ordinary alcohol and drying in the water-oven, at 228 5°:—

0·2141 gram gave 0·5708 gram CO_2 and 0·0944 gram H_2O.
0·1227 „ 15·5 c.c. moist N at 14·5° C. and 759·2 mm. bar.

	Calculated for $C_{23}H_{16}N_4O_2$.	Found.
C	72·63	72·70
H	4·21	4·89
N	14·73	14·80

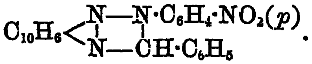
Subsequent preparations of this triazine were always crystallised from methylated spirit. Long cohobation with the solvent is necessary before the solution is saturated, and the rhombic crystals separate but slowly on allowing the solution to stand. We have not yet been able to obtain crystals sufficiently well defined for measurement. In the course of our experiments we have again met with an apparent isomerism, or crystalline allotropy, of a similar character to that observed in the orthonitrotriazine. The difference in this case is revealed by a difference in solubility, the less soluble modification forming small, opaque, yellowish crystals which are apparently rhombic, but much smaller and less soluble than the large, transparent crystals of the more soluble modification. The difference in solubility is observed only when a low boiling-point solvent, such as methylated spirit, is used. The opaque, insoluble modification melts at a lower temperature, viz., 225—226°. Analysis gave the following result:—

0·1782 gram gave 21·6 c.c. N at 10·5° C. and 777·3 mm. bar.

	Calculated.	Found.
N	14·73	14·80

The transparent, rhombic crystals gradually undergo spontaneous transformation into the opaque, yellow form; light probably facilitates the change. The melting point of a specimen which had been exposed for some weeks, and which had been observed to undergo this change, was found to be 226°.

Az-p-Nitrophenyl-*ald*-phenylnaphthotriazine,



$$C_{10}H_6<\begin{matrix}N—N\cdot C_6H_4\cdot NO_2(p)\\ |\quad\quad | \\ N—CH\cdot C_6H_5\end{matrix}.$$

This compound was prepared in the usual way, and crystallised from alcohol, in which it dissolves but slowly, and separates from the solution, on long standing, in well-defined crystals. The substance dissolves uniformly, and no insoluble or opaque modification was observed, as in the case of the other isomerides. The melting point is not very well defined, as the substance decomposes on heating; it begins to shrink at 235°, and melts with blackening at about 243°. The purity of the compound was established by analysis:—

0·2202 gram gave 0·5839 gram CO_2 and 0·0865 gram H_2O.
0·1295 „ 16·3 c.c. moist N at 13·3° C. and 757·2 mm. bar.

	Calculated for $C_{23}H_{16}N_4O_2$.	Found.
C..............	72·63	72·32
H	4 21	4·36
N	14·73	14·78

The crystallographic characters have been studied by Mr. W. J. Pope, of the Central Institution, who has been good enough to supply us with the following determinations:—

" Crystalline system. Monosymmetric.

$$a : b : c = 1·5154 : 1 : 1·2212.$$

$$\beta = 57° 42'.$$

Forms observed—

a .... $\{100\}$
b .... $\{010\}$
c .... $\{001\}$
d .... $\{\bar{1}01\}$
m .... $\{011\}$

FIG. 1.

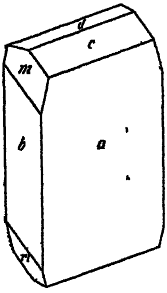
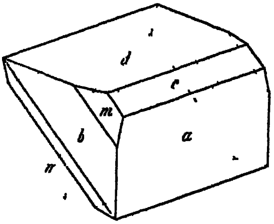


FIG. 2.



Angle.		Number of observations	Limits	Mean.	Calculated.
ac	100 : 001	30	55° 18′— 59° 11′	57° 49′	57° 42′
cd	001 : $\bar{1}$01	17	50 0 — 50 12	50 6	—
ad	$\bar{1}$00 : $\bar{1}$01	21	71 39 — 72 16	71 55	72 11
bm	010 : 011	22	38 47 — 41 37	40 35	40 42
mc	011 : 001	25	48 58 — 52 21	49 18	—
dm	$\bar{1}$01 : 011	6	65 7 — 65 48	65 25	65 18
dm	$\bar{1}$01 : 01$\bar{1}$	3	114 46 —114 54	114 49	114 42
am	100 : 011	13	69 18 — 69 53	69 36	—
am	$\bar{1}$00 : 011	12	110 14 —110 48	110 27	110 14
bd	010 : $\bar{1}$01	12	89 34 — 90 30	89 58	90 0
ab	100 : 010	16	88 45 — 91 43	90 4	90 0

This substance generally crystallises from alcohol in the form of small, transparent, brownish tables (Fig. 1), but crystals are often found in which parallel faces of the forms *a*{100}, *c*{001}, and *d*{$\bar{1}$01} are very unequal in size, giving rise to the peculiar wedge-shaped crystal represented in Fig. 2.

The pinacoids *a* and *b* are generally the largest faces on the crystal; the form *a*{100} is much striated parallel to the prism edge *ab*; *m*{011} is fairly bright, and more perfect than *c*{001} and *d*{$\bar{1}$01}. The form *b*{010} is bright, and not striated.

The crystals sometimes show only the pinacoids *a*{100}, *b*{010}, and *c*{001}.

There is an imperfect cleavage parallel to *b*(010); the crystals are very brittle and slightly dichroic.

The optic axial plane is (010). There is a very strong dispersion, the extinctions observed through a section parallel to (010) being as follows:—

For yellow (Na) light, 2° 40′ to the edge *bc*, and 47° 25′ to the adjacent edge *db*.

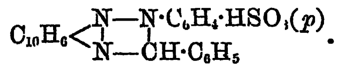
For green (Tl) light, 5° 30′ to the edge *bc*, and 44° 35′ to the adjacent edge *db*.

Double refraction strong.

Owing to the small size of the crystals, no further optical measurements could be made."

The nitrotriazines, ortho-, meta-, and para-, are distinctly basic; they all dissolve in hot alcohol mixed with hydrochloric acid, and the hydrochlorides separate out on cooling, especially when excess of hydrochloric acid is present. The ortho-compound forms a hydrochloride consisting of silvery scales; the hydrochloride of the meta-nitro-compound forms slender, white needles, and that of the para-nitro-compound long, prismatic needles. The acid is expelled from these salts at a temperature of 145°. The analyses generally indicated monohydrochlorides of the formula $C_{23}H_{16}N_4O_2,HCl$. Some of the preparations gave a higher percentage of chlorine than is required by this formula, indicating a tendency to retain a second molecule of hydrogen chloride.

Az-p-SULPHOPHENYL-*ald*-PHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{matrix} N—N\cdot C_6H_4\cdot HSO_3(p) \\ | \qquad | \\ N—CH\cdot C_6H_5 \end{matrix}.$$

The azo-compound required for the preparation of this triazine was obtained by the action of diazosulphanilic acid on β-naphthylamine (Griess, *Ber.*, 1882, **15**, 2191). We have found it possible to obtain a much larger yield than is given by Griess's original method by the following modification of the process:—

The sulphanilic acid is diazotised in the usual manner, and mixed with the theoretical quantity of β-naphthylamine dissolved in dilute hydrochloric acid. After standing for some hours, sufficient sodium acetate is dissolved in the solution to replace all free hydrochloric acid by acetic acid and ammonia is then gradually added till the solution is faintly alkaline. The deep orange solution is then slowly raised to the boiling point, and calcium chloride solution added to slight excess, the contents of the vessel being then set aside for some hours till quite cold. The calcium salt is thus obtained as a pulp of fine, orange, needle-shaped crystals. These are collected, washed well with cold water, decomposed by boiling with a solution of potassium carbonate, the calcium carbonate filtered off, and the solution evaporated to the crystallising point. The crystalline potassium salt is then decomposed by dilute hydrochloric acid, and the free azo-sulphonic acid collected, washed, and dried.

The conversion of the azo-compound into the triazine is effected in the usual way by heating with glacial acetic acid and benzaldehyde. The azo-compound does not actually dissolve in this case, but this does not appear to interfere with the reaction. The triazine, when formed, does not dissolve, as it possesses acid instead of basic properties, but it remains as a heavy, white, crystalline deposit suspended in acetic acid. The crude product was purified by collecting it on a filter, washing with glacial acetic acid till free from colour, then washing with water, and drying. The dry substance was then powdered and boiled repeatedly with alcohol, this treatment having been found necessary to remove a retained trace of some impurity which interfered with the analytical results, the percentage of nitrogen being somewhat low before such alcoholic extraction. The triazine was finally obtained in a condition suitable for analysis by dissolving it in hot, dilute ammonia, filtering, and decomposing the ammonium salt by hydrochloric acid. The sulphotriazine separates at first as a bulky, white jelly, but on standing it gradually shrinks, and becomes dense and crystalline. The crystals are ill-defined, and appear to consist of irregular plates. The substance has no definite melting point, but blackens at about 250—260°. It contains water of crystallisation, which is not expelled at 125°. A specimen dried at 110° till constant in weight, and then at 125° for 1½ hours till constant, lost only 0·88 per cent.; the loss calculated for 1 mol. of water being 4·1 per cent., and for ½ mol. 2·1 per cent.

The greatest difficulty has been experienced in getting satisfactory results by the analysis of the free acid. Large numbers of combustions have been made, all of which tend to show that the compound retains irregular quantities of water. The difficulty is, moreover, increased by the necessity of using lead chromate and the consequent formation of oxides of nitrogen. The attached water appears to be removed by prolonged and repeated cohobation with alcohol, in the manner described above as necessary for the purification of the compound. The only satisfactory numbers obtained were given by the analysis of preparations treated in this way:—

0·2272 gram gave 0·5503 gram CO_2 and 0·0927 gram H_2O.
0·1860 „ 15·1 c.c. moist N at 12° C. and 769·3 mm. bar.
0·1538 „ 0·0873 gram $BaSO_4$.

	Calculated for $C_{23}H_{17}N_3SO_3$.	Found.
C	66·50	66·05
H	4·09	4·53
N	10·12	9·74
S.............	7·71	7·79

The analyses of preparations, before treatment with alcohol, gave results varying from $C_{23}H_{17}N_3SO_3,H_2O$ to $C_{23}H_{17}N_3SO_3,\frac{1}{4}H_2O$.

The triazinesulphonic acid is almost insoluble in water and alcohol;

it possesses a taste which is at first bitter, and then intensely sweet. Its salts are also sweet. The potassium and sodium salts separate as white needles when the acid is dissolved in potash or soda, and an excess of the alkali added to the solution. The alkaline and alkaline earth salts of the acid tend to come out in a gelatinous condition at first, and become crystalline on standing. The calcium salt was prepared by adding calcium chloride to a hot aqueous solution of the neutral ammonium salt of the sulphonic acid. A white, gelatinous precipitate separated, which soon changed into a pulp of fine, white needles. After one crystallisation from boiling water, the salt was analysed :—

0·1688 gram gave 0·0248 gram $CaSO_4$.
0·4563 „ dried at 100°, lost 0·0333 gram on heating to 145° for three hours, by which time the weight was constant.

	Calculated for $[C_{23}H_{16}N_3SO_3]_2Ca,4H_2O$.	Found.
Ca	4·25	4·31
H_2O	7 66	7·29

The barium salt was prepared in a similar way, and forms a woolly mass of fine, white needles when dry.

0·1524 gram gave 0·0353 gram $BaSO_4$.
0·3052 „ dried at 100°, lost 0·0102 gram when heated to 145°, till the weight was constant.

	Calculated for $[C_{23}H_{16}N_3SO_3]_2Ba,2H_2O$.	Found.
Ba	13·68	13·61
H_2O	3·59	3·34

Many other salts were prepared in the same manner :—

Zinc Salt.—Prepared by adding zinc sulphate to the solution of the ammonium salt. Gelatinous at first; afterwards changes to white needles, soluble in boiling water.

Lead Salt.—By adding lead acetate to the ammonium salt. Amorphous, white precipitate, soluble in boiling water, and separating, on cooling, in an amorphous form.

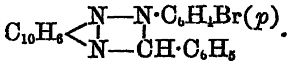
Cobalt Salt.—From cobalt nitrate and the ammonium salt. Rosettes of white needles, soluble in boiling water.

Nickel Salt.—From nickel sulphate and the ammonium salt. Similar in appearance and properties to the foregoing.

Copper Salt.—From copper sulphate and the ammonium salt. An amorphous, white powder, insoluble in water.

Manganese Salt.—From manganese chloride and the ammonium salt. Opaque, whitish needles, soluble in boiling water.

Az-p-BROMPHENYL-*ald*-PHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{array}{l}N—N\cdot C_6H_4Br(p)\\ \,|\qquad |\\ N—CH\cdot C_6H_5\end{array}.$$

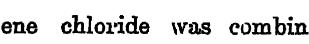
The azo-compound was prepared by the action of diazotised parabromaniline on β-naphthylamine hydrochloride in the usual way. On adding sodium acetate to the mixed solutions, the compound slowly separates as a cake of dense red resin. After crystallisation from alcohol, the pure parabrombenzeneazo-β-naphthylamine was obtained in the form of beautiful, red, prismatic needles, having a melting point of 135°. From the latter the triazine was prepared in the usual way. After being twice crystallised from alcohol, the compound was pure, forming colourless prisms, which begin to darken at 195°, and fuse at 211° to a dark-green oil, which dissolves in alcohol with a bluish-green colour. Analysis gave the following results:—

0·2310 gram gave 0·5632 gram CO_2 and 0·0855 gram H_2O.
0·1358 „ 12·2 c.c. moist N at 21° C. and 756 mm. bar.
0·2813 „ 0·1310 gram AgBr.

	Calculated for $C_{23}H_{16}N_3Br$.	Found.
C	66·66	66·49
H	3·86	4·11
N	10·14	10·16
Br	19·32	19·81

The crystals of this triazine do not appear to undergo transformation into an opaque form on heating, nor have we been able to obtain two modifications by crystallisation from alcohol or any other solvent.

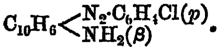
Az-p-CHLORPHENYL-*ald*-PHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{array}{l}N—N\cdot C_6H_4Cl(p)\\ \,|\qquad |\\ N—CH\cdot C_6H_5\end{array}.$$

Diazo-*p*-chlorbenzene chloride was combined with β-naphthylamine, dissolved in dilute hydrochloric acid, in the usual manner. On adding sodium acetate, the azo-compound separates out as a red resin, which dissolves readily in boiling alcohol, and separates on cooling in the form of long, orange-red needles. After two crystallisations, the melting point was constant, viz., 116°, and the substance, which does not appear to have been described, was analysed:—

0·1679 gram gave 21 c.c. moist N at 12° C. and 767·4 mm. bar.

	Calculated for  $C_{10}H_6{<}\begin{smallmatrix}N_2\cdot C_6H_4Cl(p)\\ NH_2(\beta)\end{smallmatrix}$.	Found.
N	14·92	14·97

The triazine dissolves readily in hot alcohol, and separates, if the solvent is diluted with a little water, in bundles of glistening, white needles, melting at 211—212°, and decomposing with the formation of a dark-green oil, similar to that resulting from the decomposition of the corresponding bromtriazine. The crystals which separated from dilute alcohol, after drying in the water-oven, gave the following result:—

0·1243 gram gave 12·2 c.c. moist N at 14·5° C. and 762·2 mm. bar.

	Calculated for $C_{23}H_{16}N_3Cl$.	Found.
N	11·37	11·53

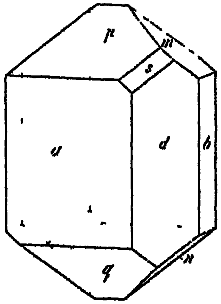
If instead of dilute alcohol strong alcohol is used as a solvent, the triazine slowly separates in the form of large, transparent crystals; these were submitted to Mr. W. J. Pope for measurement:—

"Crystalline system. Anorthic.

$$a : b : c = 0{\cdot}8830 : 1 : 0{\cdot}7757.$$

$$\alpha = 89^\circ\ 21'. \quad \beta = 88^\circ\ 45'. \quad \gamma = 85^\circ\ 49'.$$

FIG. 3.



Forms observed—

a	{100}
b	{010}
d	{110}
m	{011}
n	$\{0\bar{1}1\}$
p	{101}
q	$\{\bar{1}01\}$

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.
ad = $100 : 110$	21	39° 9′— 10° 26′	39° 41′	—
ad = $\bar{1}00 : 110$	4	110 14—110 26	140 21	110° 19′
bd = $010 : 110$	15	46 32— 47 3	46 50	46 8
ab = $\bar{1}00 : 010$	17	92 47— 94 40	93 6	94 11
ap = $100 : 101$	33	47 32— 48 24	47 56	—
pq = $101 : \bar{1}01$	34	82 0— 82 55	82 40	—
aq = $\bar{1}00 : \bar{1}01$	19	48 21— 50 47	49 29	49 24
bm = $010 : 011$	5	51 15— 51 54	51 31	51 40
mn = $011 : 0\bar{1}1$	7	75 2— 75 49	75 24	75 48
bn = $010 : 0\bar{1}1$	5	52 13— 53 30	52 32	52 32
dp = $110 : 101$	13	58 3— 59 1	58 36	—
pn = $101 : 0\bar{1}1$	18	55 22— 55 50	55 33	—
nd = $0\bar{1}1 : \bar{1}\bar{1}0$	24	64 50— 66 26	65 41	65 51
dm = $110\ 011$	4	64 25— 66 27	65 43	63 47
mq = $011 : \bar{1}01$	4	51 56— 55 19	55 8	55 55
qd = $\bar{1}01 : \bar{1}\bar{1}0$	16	58 48— 60 56	59 37	60 18
am = $100 : 011$	2	87 5 — 87 43	87 22	86 26
am = $\bar{1}00 : 011$	3	92 11— 92 40	92 29	93 34
mp = $011 : 101$	8	51 2— 52 3	51 25	51 3
bq = $0\bar{1}0 : \bar{1}01$	3	87 20— 87 50	87 42	87 50
bq = $010 : \bar{1}01$	2	92 27— 93 1	92 41	92 10
sp = $211 : 101$	1		(approx.) 25 38	27 40
ds = $110 : 211$	1		(approx.) 32 31	30 57

The crystals consist of small, yellow-tinted, transparent prisms (Fig. 3). The forms *a*{100} and *d*{110} are large and badly developed; the other forms are small and bright. The form *s*{211} occurs but seldom, and is very minute.

The extinctions through *a*(100) and *d*(110) are parallel to the prism edge, but the crystals are too small and too brittle to permit of sections being cut for the determination of the optical constants.

Double refraction strong. No definite cleavage.

The crystals gradually become opaque and amorphous, especially on exposure to light.

These crystals contain alcohol of crystallisation; on heating, they become white and opaque at 100°, they darken at 185°, and melt with decomposition at 206°. They become opaque and amorphous spontaneously on keeping for some time. The alcohol is expelled at 100°:—

0·4530 gram, dried in air and then in the water-oven till constant, lost 0·0503 gram.

	Calculated for $C_{23}H_{16}N_3Cl,C_2H_6O$.	Found.
C_2H_6O	11·07	11·10

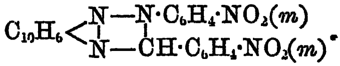
Another preparation of the triazine, which for some unknown reason had become contaminated with coloured impurities during formation, was crystallised several times from toluene, in which it dissolves freely, when the solvent is boiling, and separates on cooling as a white, crystalline cake. This specimen, when dry, had the same melting point, 206°, and gave the following results on analysis:—

0·1425 gram gave 0·3876 gram CO_2 and 0·0594 gram H_2O.
0·1620 „ 16·2 c.c. moist N at 21·5° C. and 757·6 mm. bar.

	Calculated for $C_{23}H_{16}N_3Cl$.	Found.
C	74·69	74·18
H	4·33	4·63
N	11·37	11·30

The supply of material having become exhausted, no further analyses were possible. The crystals obtained from toluene are much smaller and not so well defined as those obtained by slow crystallisation from strong alcohol.

Az-*m*-NITROPHENYL-*akl*-*m*-NITROPHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{array}{l}N-N\cdot C_6H_4\cdot NO_2(m)\\ \;|\quad\;\;|\\ N-CH\cdot C_6H_4\cdot NO_2(m)\end{array}.$$

This compound is easily prepared by heating metanitrobenzeneazo-β-naphthylamine with the calculated quantity of metanitrobenzaldehyde in glacial acetic acid. In a few minutes the solution becomes colourless, and the triazine separates as a heavy, white crystalline deposit. In order to purify the product, it was repeatedly extracted with hot alcoholic soda, by which treatment a trace of some orange colouring matter was removed. After being washed with water and dried, the substance was crystallised from boiling glacial acetic acid. It dissolves but very sparingly in this solvent, and is quite insoluble in alcohol, the benzene hydrocarbons, and other ordinary solvents. The substance possesses no basic properties, as it is undissolved by alcoholic hydrochloric acid. Neither does it possess acid properties, as it is undissolved by alcoholic soda. The crystals which separate from acetic acid are rhombic, and consist apparently of two kinds, one being light ochreous and the other slightly orange. It is possible that this indicates the same kind of isomerism or crystalline allotropy observed in the other triazines, but the crystals were inextricably mixed, and could not be separated by mechanical sorting.

Analysis revealed the fact that the crystals contained acetic acid of crystallisation:—

0·2200 gram, dried at 100°, gave 0·5005 gram CO_2 and 0·0848 gram H_2O.

0·1375 gram, dried at 100°, gave 16·99 c.c. moist N at 18° C. and 755·4 mm. bar.

0·5131 gram, dried at 100°, lost 0·0648 gram when dried at 145° till constant.

	Calculated for $C_{23}H_{15}N_5O_4,C_2H_4O_2$.	Found.
C	61·85	62·04
H	3·91	4·28
N	14·43	14·09
$C_2H_4O_2$........	12·37	12·62

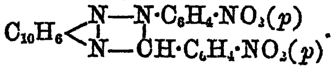
0·1609 gram, dried at 145°, gave 0·3837 gram CO_2 and 0·0573 gram H_2O.

0·1000 gram, dried at 145°, gave 14·2 c.c. moist N at 18·5° C. and 759·2 mm. bar.

	Calculated for $C_{23}H_{15}N_5O_4$.	Found.
C	64·94	65·03
H	3·53	3·95
N	16·47	16·32

The substance melts at 248—249° with blackening. The crystals, which are semi-transparent, become quite opaque on heating rapidly to 140°, and even in the water-oven gradually undergo the same change without losing acetic acid. The change is, therefore, due to crystalline modification, and is not connected with the loss of acetic acid.

Az-p-NITROPHENYL-*ald-p*-NITROPHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{matrix}N—N\cdot C_6H_4\cdot NO_2(p)\\ |\quad\quad |\\ N—CH\cdot C_6H_4\cdot NO_2(p)\end{matrix}.$$

This compound was prepared in precisely the same way as the foregoing from paranitrobenzeneazo-β-naphthylamine and paranitrobenzaldehyde. The triazine forms very rapidly, and separates from the acetic acid solution in a crystalline form. In order to purify it, the crude product was collected on a filter, washed with cold glacial acetic acid, and crystallised from the same solvent. The substance is practically insoluble in alcohol, and boiling glacial acetic acid was the only solvent that could be conveniently used. From this solution, the triazine separates on cooling in two distinct forms, viz., opaque, sulphur-yellow needles, and minute, dull, orange, rhombic crystals, the latter being present only in small quantity. The melting points were:—

Yellow needles........	267° with blackening.
Rhombic crystals	269—270° with blackening.

The rhombic crystals were not present in sufficient quantity to enable the complete separation of the two forms to be effected by mechanical sorting. After some trouble, enough of each was obtained for analysis, and the results showed that the yellow needles were free from acetic acid, whilst the rhombic crystals contained 1 mol. of this acid:—

0·1460 gram (yellow needles) gave 0·3479 gram CO_2 and 0·0553 gram H_2O.

0·1314 gram (yellow needles) gave 18·9 c.c. moist N at 20·5° C. and 758·3 mm. bar.

	Calculated for $C_{23}H_{15}N_5O_4$.	Found.
C	64·94	64·98
H	3·53	4·20
N	16·47	16·43

The fact that this form contains no acetic acid was established by drying a weighed specimen at 145°; the loss was only 0·23 per cent.

0·0484 gram (rhombic crystals) dried at 145° gave 6·9 c.c. moist N at 19° C. and 752·8 mm. bar.

	Calculated for $C_{23}H_{15}N_5O_4$.	Found.
N	16·47	16·20

0 0575 gram (rhombic crystals), dried at 145°, till constant lost 0·0070 gram.

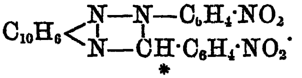
	Calculated for $C_{23}H_{15}N_5O_4,C_2H_4O_2$.	Found.
$C_2H_4O_2$	12·37	12·17

The rhombic crystals are small and ill-defined, and not capable of being measured; they become quite opaque at 140°. A specimen of the mixed crystals before separation, dried at 145°, gave the following results:—

0·1509 gram gave 0·3600 gram CO_2 and 0·0510 gram H_2O.

	Calculated.	Found.
C	64·94	65·06
H	3·53	3·75

While the mononitrotriazines are, as already stated, sufficiently basic to form hydrochlorides, and the dimetadinitro-compound, above described, neither basic nor acid, the present diparadinitrotriazine is distinctly acid. It dissolves readily in cold alcoholic soda with a reddish-brown colour, and is reprecipitated unaltered by acids. The substance is not reduced in alkaline alcoholic solution by prolonged heating with ammonium sulphide; when heated for some hours with zinc-dust, the alkaline alcoholic solution is decolorised, but the original colour is rapidly restored on exposure to the air. A dihydro-derivative is probably formed at this stage. On continuing the heating with alcoholic soda and zinc-dust for some days, the triazine is reduced completely with the formation of amorphous, uncrystallisable products which have not been further examined. No definite salts of this acid triazine have as yet been obtained. The replaceable hydrogen is, doubtless, the atom* belonging to the aldehydo residue:—



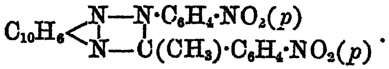
$$C_{10}H_6<\begin{array}{l}N-N-C_6H_4\cdot NO_2\\ \mid\quad\;\;\mid\\ N-\underset{*}{C}H\cdot C_6H_4\cdot NO_2\end{array}.$$

By cohobating some of the substance with the calculated quantity of sodium hydroxide and methyl iodide in alcoholic solution, a methyl derivative has been prepared. The methylation is not complete by this method, but the unaltered triazine is easily removed by washing with alcoholic soda till the washings are colourless. The methyl derivative is then left as a yellow, crystalline powder. After being washed with water, cold alcohol, and then dried, the product was crystallised from glacial acetic acid diluted with a little water. After being collected and dried in the water-oven, the crystals were analysed:—

0·1350 gram gave 0·3267 gram CO_2 and 0·0491 gram H_2O.
0·1781 „ 24·8 c.c. moist N at 20° C. and 765·4 mm. bar.

	Calulated for $C_{24}H_{17}N_5O_4$.	Found.
C	65·60	65·99
H	3·87	4·03
N	15·94	16·02

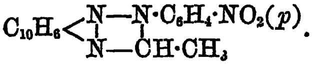
The compound forms beautiful fern-like crystals of a dull yellow colour; it is but very slightly soluble in alcohol. Its constitution is no doubt expressed by the formula:—



$$C_{10}H_6<\begin{array}{l}N-N\cdot C_6H_4\cdot NO_2(p)\\ \mid\quad\;\;\mid\\ N-C(CH_3)\cdot C_6H_4\cdot NO_2(p)\end{array}.$$

The same product might perhaps be obtained by the condensation of paranitrophenyl-methyl-ketone with paranitrobenzeneazo-β-naphthylamine.

Az-p-NITROPHENYL-*ald*-METHYLNAPHTHOTRIAZINE,



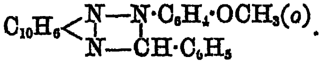
$$C_{10}H_6<\begin{matrix}N-N\cdot C_6H_4\cdot NO_2(p)\\ |\qquad | \\ N-CH\cdot CH_3\end{matrix}.$$

The investigation of this compound is not yet complete, owing to want of material, and the description now given is to be regarded as preliminary to a further study. The triazine was prepared by cohobating paranitrobenzeneazo-β-naphthylamine in glacial acetic acid with a slight excess of acetaldehyde till the original colour of the solution had nearly disappeared. On pouring the contents of the flask into water, the triazine remains in solution, owing to its basic character, and is not precipitated till the excess of acetic acid is nearly neutralised by caustic soda. The crude product when dry was purified by first extracting it with hot toluene, in which the triazine is almost insoluble; by this treatment a resinous impurity was removed. The purified substance was then dried and crystallised from alcohol. It separates slowly from the alcoholic solution, partly in the form of rosettes of thick, ochreous prisms, and partly as an oil which only solidifies on long standing, and which is apparently a compound of the triazine with alcohol. The prismatic crystals melt at about 107°. The analyses of these crystals indicated that they also contained alcohol of crystallisation:—

I. 0·1167 gram gave 0·2823 gram CO_2 and 0·0582 gram H_2O.
II. 0·0984 „ 0·2359 „ „ 0·0477 „

	Calculated for $C_{18}H_{11}N_4O_2,C_2H_6O$.	Found.	
		I.	II.
C............	65·93	65·97	65·40
H	5·49	5·54	5·38

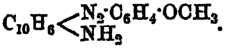
Az-o-METHOXYPHENYL-*ald*-PHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{matrix}N-N\cdot C_6H_4\cdot OCH_3(o)\\ |\qquad | \\ N-CH\cdot C_6H_5\end{matrix}.$$

The azo-compound was prepared by combining diazotised anisidine with β-naphthylamine in dilute hydrochloric acid solution in the usual way. The pure compound, after crystallisation from alcohol, forms beautiful orange scales melting at about 129°:—

0·1879 gram gave 25·2 c.c. moist N at 21° C. and 754·7 mm. bar.

	Calculated for  $C_{10}H_6<\begin{matrix}N_2\cdot C_6H_4\cdot OCH_3\\ NH_2\end{matrix}$.	Found.
N............	15·16	15·14

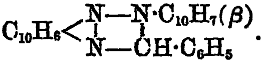
The triazine forms very readily by heating the above compound with acetic acid and benzaldehyde. After two or three crystallisations from alcohol diluted with a little water, it was obtained in the form of beautiful, transparent leaflets having a fern-like structure. The crystals are almost colourless, and have a melting point of 167°:—

0·1358 gram gave 0·3947 gram CO_2 and 0·0666 gram H_2O.
0·1002 „ 10·2 c.c. moist N at 19·5 C. and 765·8 mm. bar.

	Calculated for $C_{24}H_{19}N_3O$.	Found.
C	78·90	79·26
H	5·20	5·44
N	11·50	11·74

This triazine is characterised by its ready solubility in alcohol as compared with the other triazines hitherto prepared. The specimen used for analysis was dried in the water-oven.

Az-β-NAPHTHYL-*ald*-PHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{array}{l}N-N\cdot C_{10}H_7(\beta)\\ N-CH\cdot C_6H_5\end{array}.$$

Amidoazo-β-naphthalene is easily prepared by adding a solution containing the calculated quantity of sodium nitrite (1 mol.) to a solution of β-naphthylamine (2 mols.) in dilute hydrochloric acid. The azo-compound is readily transformed into the triazine by the process described. The crude product, after being precipitated, washed, and dried, forms an ochreous powder readily soluble in alcohol and benzene, but very difficult to crystallise as long as the smallest trace of impurity is present. The only solvent which gave satisfactory results for first crystallisation was methyl alcohol. From this the triazine separates in the form of rosettes of transparent, ochreous needles which contain methyl alcohol. The substance on heating begins to lose its transparency at 100°, and is quite opaque at 120°. At 203°, it fuses to a dark-green oil. A specimen recrystallised from toluene formed tufts of stumpy, white needles melting at 204—205°. The substance, dried in air, further dried at 150° till constant, with the following result:—

0·4283 gram lost 0·0147 gram.

	Calculated for $C_{27}H_{19}N_3,\frac{1}{2}CH_4O$.	Found.
CH_4O	3·99	3·43

For analysis the compound crystallised from methyl alcohol and dried at 140° was used:—

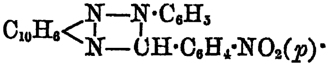
0·1271 gram gave 0·3904 gram CO_2 and 0·0605 gram H_2O.
0·1572 „ 14·6 c.c. moist N at 18·5° C. and 762·3 mm. bar.

	Calculated for $C_{27}H_{19}N_3$.	Found.
C	84·15	83·75
H	4·93	5·27
N	10·91	10·72

Although the crystals obtained by slow crystallisation from dry methyl alcohol are semi-transparent, if the solvent contains water, the substance separates in the form of opaque, white needles.

In order to study the influence of the position of the nitro-group upon the properties of the triazines, we have prepared for comparison with the mononitro-triazines, previously described, a pair of isomeric compounds containing the nitro-group in the aldehyde residue.

Az-PHENYL-*ald*-*p*-NITROPHENYLNAPHTHIOTRIAZINE,



$$C_{10}H_6<\begin{matrix}N—N\cdot C_6H_5\\ \mid \quad\ \ \mid \\ N—CH\cdot C_6H_4\cdot NO_2(p)\end{matrix}$$

By heating a solution of benzeneazo-β-naphthylamine in glacial acetic acid with the calculated quantity of paranitrobenzaldehyde, the triazine separates out in a few minutes in the form of beautiful, yellow, rhombic prisms. The fact that the triazine separates from the acetic acid solution is immediate evidence showing that this compound is less basic than the isomeric compound containing the *az*-*p*-nitro-group. The substance, after crystallisation from alcohol, forms fine needles of a sulphur-yellow colour melting with blackening at 228—229°. The substance dried in the water-oven gave the following results:—

0·1355 gram gave 0·3600 gram CO_2 and 0·0557 gram H_4O.
0·1286 „ 16·8 c.c. moist N at 20° C. and 755·3 mm. bar.

	Calculated for $C_{23}H_{16}N_4O_2$.	Found.
C	72·63	72·45
H	4·21	4·56
N	14·73	14·83

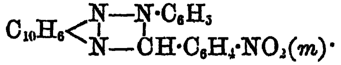
The substance crystallised from acetic acid retains some of the solvent, as in the case of the dinitrotriazines:—

0·1002 gram dried at 100° gave 12 c.c. moist N at 20° C. and 760·7 mm. bar.

	Calculated for $C_{23}H_{16}N_4O_2,\frac{1}{2}C_2H_4O_2$.	Found.
N	13·65	13·69

An attempt was made to determine the acetic acid, but it was found that the whole of the acid was not expelled on prolonged heating at 145—150°. The crystals of this compound are homogeneous.

Az-PHENYL-*ald*-*m*-NITROPHENYLNAPHTHOTRIAZINE,



$$C_{10}H_6<\begin{matrix}N—N\cdot C_6H_5\\ | \quad\quad | \\ N—CH\cdot C_6H_4\cdot NO_2(m)\end{matrix}.$$

This compound was prepared by the usual method of heating benzeneazo-β-naphthylamine with acetic acid and metanitrobenzaldehyde. The triazine forms very rapidly, and separates from the acetic acid in the form of whitish, prismatic needles. The substance was recrystallised from glacial acetic acid, and was thus obtained in the form of straw-coloured, prismatic needles melting with blackening at 212°, and retaining acetic acid after drying in the water-oven. A specimen thus dried was analysed with the following results:—

0·1477 gram gave 0·3875 gram CO_2 and 0·0617 gram H_2O.
0·1133 ,, 14 3 c.c. moist N at 20·5° C. and 757·1 mm. bar.
0·2674 gram, dried at 140—145° till constant, lost 0·0094 gram.

	Calculated for $C_{23}H_{16}N_4O_2,\frac{1}{4}C_2H_4O_2$.	Found.
C	71·40	71·54
H	4·30	4·64
N	14·17	14·33
$\frac{1}{4}C_2H_4O_2$..	3·80	3·51

The substance dried at 140—145° gave the following results:—

0·1320 gram gave 0·3535 gram CO_2 and 0·0533 gram H_2O.
0·1022 ,, 13·2 c.c. moist N at 18·5° C. and 761·4 mm. bar.

	Calculated for $C_{23}H_{16}N_4O_2$.	Found.
C	72·63	73·02
H	4·21	4·48
N	14·73	14·89

Crystallisation from alcohol, as in the case of the isomeric *ald*-*p*-nitro-compound, deprives the substance of its acetic acid. It then forms silky, straw-coloured needles melting with blackening at 215°:—

0·1094 gram gave 14·2 c.c. moist N at 20° C. and 762·6 mm. bar.

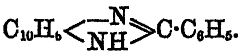
	Calculated.	Found.
N	14·73	14·88

This substance is less basic than its isomeride, and is also less soluble in alcohol and other solvents. Its crystalline form appears to be likewise homogeneous.

Reduction of the Nitrotriazines.*

During the course of the preceding investigation, a large amount of time has been devoted to the study of the products of reduction of the nitrotriazines. This part of the work has presented the greatest difficulty, especially in the case of the metanitrotriazine, owing to the complex nature of the products, the difficulty of separating them, and the uncrystallisable character of some of the compounds. After much labour we have, however, succeeded in giving a very good account of these products; and, although we cannot consider this part of the subject to be absolutely complete, the ground has been so far cleared by our experiments that the subsequent study of these products can be resumed with a substantial basis of facts to start from.

It was anticipated in commencing this branch of the investigation, that the mild reduction of these compounds would have given bases resulting simply from the amidation of the nitro-group, *i.e.*, amidotriazines. It was soon found, however, that the transformation in the case of triazines containing an *az*-nitro-group was of a more radical character, the whole complex of nitrogen and carbon atoms breaking down and recombining under the influence of the reducing agent. The detailed results are given below, but the one general result obtained with the ortho-, meta-, and para-nitrotriazines may be conveniently referred to first. Under suitable conditions these three compounds all give the anhydro-base, benzenyl-α-β-naphthylenediamine:—



$$C_{10}H_6{<}\genfrac{}{}{0pt}{}{\text{—N}}{\text{NH}}{>}C\cdot C_6H_5.$$

This base was first obtained by Ebell (*Annalen*, **208**, 328), but he erroneously describes it as crystallising in yellow needles, whereas our preparations were always white. Our identification of the base was delayed for this reason till the compound was recently redescribed by Koll (*Annalen*, **263**, 313), with whose description our substance completely agrees.

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* We received much assistance in this part of the work from Mr. F. S. Bayley, to whom we take the present opportunity of recording our thanks.

It is not easy to see at first how the anhydro-base is formed from the nitrotriazine, as the conditions under which anhydro-bases are usually formed on reduction are not obviously present. It will be seen, however, from the results, that the oxygen of the nitro-group is the effective oxidiser in this case. The mechanism of the transformation will be best considered after the experimental evidence has been submitted.

Reduction of the az-o-*Nitrophenyl Derivative.*

The substance was dissolved in alcohol with the addition of strong hydrochloric acid, and zinc-dust was added to the warm solution, which was allowed to stand, with frequent agitation, for about an hour. The solution was then filtered, and the filtrate diluted with water till a white substance began to separate. It was found that the addition of strong hydrochloric acid greatly promoted the separation of the compound. The latter consisted of fine, white needles, and proved to be the hydrochloride of the anhydro-base. We may remark that the insolubility of the hydrochloride of this base in the presence of hydrochloric acid is a most characteristic property. The salt is but slightly soluble in cold water, but dissolves more freely in boiling water; in the presence of an excess of acid, it is but slightly soluble, even when the solution is boiling. The base obtained from this salt had the properties ascribed to it by Koll; m. p. 214°:—

0·1278 gram gave 12 c.c. moist N at 12° and 776·6 mm. bar.

	Calculated for $C_{17}H_{12}N_2$.	Found.
N	11·47	11·37

Under the conditions of the experiment, the orthonitrotriazine passes at once into the anhydro-base; no intermediate product was detected. The action of the reducing agent may be represented by the following equation:—

$$C_{23}H_{16}N_4O_2 + 4H_2 = C_{17}H_{12}N_2 + C_6H_4(NH_2)_2 + 2H_2O.$$

Reduction of the az-p-*Nitrophenyl Derivative.*

The reduction of this triazine was studied under various conditions, as we had a considerable quantity of the material to work with. Mild reduction was first tried in the following way.—The substance was dissolved in hot glacial acetic acid, and the solution diluted with about twice its volume of alcohol. When cold, zinc-dust was added, and the solution kept cool by immersing the flask in water, the action of the reducing agent being promoted by occasional agitation. After about an hour, the solution was filtered and diluted with water; the white, flocculent precipitate thus obtained was collected, washed well with water, and then basified by dilute ammonia. The dry base was crystallised from dilute alcohol, and obtained in the form of white needles. The analysis and melting point agreed approximately with the anhydro-base, but showed that the substance was not quite pure. It was therefore dissolved in boiling toluene, in which it is not very readily soluble, and allowed to crystallise. The substance separates from this solvent in the form of warty aggregates of stumpy needles of a brownish colour. The base was pure after this treatment; m. p. 214°:—

0·1000 gram gave 9·7 c.c. moist N at 14·5° and 764·2 mm. bar.

	Calculated for $C_{17}H_{13}N_3$.	Found.
N	11·47	11·43

It appears, therefore, that even with a mild reducing agent, such as zinc-dust and acetic acid in cold alcoholic solution, the paranitrotriazine passes at once into the anhydro-base.

Further experiments on the reduction of the compound in alcoholic solution with zinc-dust and hydrochloric acid were carried out, as this method was found to give the anhydro-base in quantitative yield, and we can recommend it for the preparation of this base in large quantities. The mode of procedure is the same as that described above, hydrochloric being substituted for acetic acid; there is no necessity for keeping the solution cool during the reduction. The crude hydrochloride, which separates out as a white, crystalline pulp on diluting the alcoholic filtrate with water, can be recrystallised from a large volume of boiling water, or, after washing, it may be basified, the base dissolved in alcohol, and hydrochloric acid added to the hot alcoholic solution. The salt separates out on cooling in the form of white, silky needles. For final purification, it is best to rebasify and crystallise the dry base from toluene as described. Specimens of the pure base thus prepared gave the following results:—

I.	0·1728	gram gave	0·5307	gram CO_2 and	0·0788	gram H_2O.
II.	0·1938	,,	0·5942	,,	0·0871	,,
III.	0·2045	,,	0·6266	,,	0·0924	,,
IV.	0·1383	,,	13·8 c.c. moist N at 12·2° C. and 752 mm. bar.			

	Calculated for $C_{17}H_{12}N_2$.	Found.			
		I.	II.	III.	IV.
C	83·61	83·75	83·61	83·56	—
H	4·92	5·06	4·99	5·02	—
N	11·47	—	—	—	11·69

Specimens of the pure hydrochloride gave the following results:—

0·1517 gram gave 0·4025 gram CO_2 and 0·0703 gram H_2O.
0·1269 „ 10·4 c.c. moist N at 10·5° C. and 775·4 mm. bar.
0·2100 gram, burnt with lime, gave 0·1034 gram AgCl.

	Calculated for $C_{17}H_{12}N_2,HCl$.	Found.
C	72·72	72·35
H	4·63	5·15
N	9·98	9·98
Cl	12·65	12·19

The aqueous and alcoholic solutions of the hydrochloride have a slight blue fluorescence; the alcoholic solution of the base does not fluoresce. The nitrate was prepared by adding dilute nitric acid to the alcoholic solution of the base; it crystallises in white, silky needles:—

0·0805 gram gave 9·4 c.c. moist N at 19·5° C. and 765·2 mm. bar.

	Calculated for $C_{17}H_{12}N_2,HNO_3$.	Found.
N	13·68	13·45

The base crystallised from methyl alcohol was found to contain a quantity of this solvent approximating, as stated by Koll, to $\frac{1}{2}CH_4O$.

Reduction of the az-m-*Nitrophenyl Derivative.*

The products of reduction of this triazine are more complex in character than those of either of the preceding compounds, and their investigation has entailed a very large amount of labour. The results have, however, justified the expenditure of time which has been bestowed upon them, as considerable light has been thrown by their study on the way in which the triazine ring breaks down under the influence of nascent hydrogen.

Three distinct compounds have been isolated from the products of reduction of this nitrotriazine, viz.:—(1) The anhydro-base; (2) an azoxy-compound; and (3) the amidotriazine. By the action of zinc-dust and hydrochloric acid on the nitrotriazine at the boiling point of the solvent, the chief product is the anhydro-base. At a lower temperature, a mixture of the anhydro-base and the amidotriazine is formed. The separation of these two compounds is not easily effected, and we have not yet succeeded in obtaining any quantity of the amidotriazine in a state of purity, although we have no doubt as to its being formed under the conditions specified. The experiments which have led to this conclusion were conducted in the following way:—

The nitrotriazine was dissolved in hot alcohol, with the addition of an excess of hydrochloric acid. When cold, zinc-dust was added, and the solution briskly agitated, care being taken not to let the contents of the flask get more than perceptibly warm to the hand. When the reduction was complete, the solution was filtered, and then diluted with water. An excess of sodium acetate was then added, the addition of this salt causing the separation of a bulky, white, curdy precipitate. The latter was collected, washed with water till free from soluble salts, and then extracted with cold dilute hydrochloric acid, and filtered. The residue consisted of the hydrochloride of the anhydro-base. After crystallisation from alcohol and boiling water successively, it was analysed, with the following results:—

0·0974 gram, dried at 100°, gave 7·6 c.c. moist N at 11·5° C. and 754 mm. bar.

1·0614 gram, dried at 100°, and then at 110° till constant, lost 0 0919 gram.

	Calculated for $C_{17}H_{12}N_2,HCl,1\frac{1}{2}H_2O$.	Found.
N	9·10	9·19
H_2O	8·78	8·66

The hydrochloride crystallised from water thus retains water of crystallisation, a fact not hitherto noticed in connection with this salt. A specimen deprived of its water by drying was also analysed:—

0·2339 gram gave 0·6245 gram CO_2, and 0·1072 gram H_2O.

0·1536 „ 12·9 c.c. moist N at 10·3° C. and 746·5 mm. bar.

0·1709 gram, burnt with lime, gave 0·0864 gram AgCl.

	Calculated for $C_{17}H_{12}N_2,HCl$.	Found.
C	72·72	72 81
H	4·63	5·09
N	9·98	9·85
Cl	12·65	12·50

The free base had the properties already ascribed to it.

The filtrate containing the portion dissolved by cold dilute hydrochloric acid had a strong greenish fluorescence. On making alkaline with ammonia, a white, flocculent base separated; this was collected, washed, and crystallised from dilute alcohol several times. The compound was finally obtained in the form of opaque, white needles. The analyses only approximated to the numbers required by the amidotriazine, but we have no doubt that the product consists of this base mixed with some of the anhydro-base. In the course of subsequent experiments, using zinc-dust and acetic acid for reducing the nitrotriazine, we have obtained further quantities of this mixture of bases, and have been enabled to prove conclusively that the amidotriazine is one of its constituents. These experiments will be most conveniently described now.

The reduction with zinc-dust and acetic acid was effected in cold alcoholic solution in precisely the same way as with the corresponding paranitrotriazine. After precipitation by water and washing, the product was extracted with cold dilute hydrochloric acid, and thus divided into a soluble basic portion and an insoluble, ochreous residue. The base was thrown out of the filtrate by ammonia, collected, washed, redissolved in dilute hydrochloric acid, filtered, and again precipitated by ammonia. The product, after being collected and washed, was crystallised from dilute alcohol. The base formed the characteristic opaque, white needles, but was found by analysis to be impure. It was therefore crystallised from toluene, and obtained in the form of warty conglomerates of dull, whitish needles :—

0·1376 gram gave 0·4005 gram CO_2 and 0 0692 gram H_2O.
0·1043 „ 13·9 c.c. moist N at 15·5° C. and 764·4 mm. bar.

	Calculated for $C_{23}H_{16}N_3{\cdot}NH_2$.	Found.
C................	78 86	79 38
H................	5·14	5·59
N.........	16·00	15·64

These results are sufficiently close to indicate that the base extracted by cold dilute hydrochloric acid is the amidotriazine. The melting point was about 190°.

The ochreous residue left after extraction by dilute hydrochloric acid was soluble in alcohol, and on adding dilute hydrochloric acid to the hot solution, a substance crystallising in orange needles separated out on cooling. This proved to be the hydrochloride of the azoxy-compound mixed with some impurity, probably the hydrochloride of the anhydro-base. Purification was effected by basifying the product, dissolving in hot alcohol, and recrystallising by the addition of hydrochloric acid and water. After several such treatments, the product was finally basified, dried, and analysed:—

0·1730 gram gave 0·4911 gram CO_2 and 0·0751 gram H_2O.
0·0901 „ 12 c.c. moist N at 17·5° C. and 765·1 mm. bar.

	Calculated for $\begin{matrix}C_{23}H_{16}N_3\cdot N\\ C_{23}H_{16}N_3\cdot N\end{matrix}\!>\!O.$	Found.
C	77·52	77·42
H	4·49	4·82
N	15·73	15·52

This azoxy-compound forms flat, orange needles; the base, when quite pure, is very difficultly soluble in alcohol and acetic acid, but its solubility appears to be enormously increased by association with impurities. It is not improbable that the insoluble form may be some kind of isomeride resulting from the action of heat upon the substance during the process of solution. It was occasionally observed that after the impure base had dissolved in hot alcohol or acetic acid, the compound began to crystallise out, although the solution was kept boiling. Although this is apparently in favour of the explanation offered, it is also possible that the substance forms a soluble molecular compound with the anhydro-base or other impurity with which it is associated, and that it is only when this compound is resolved by the action of the hot solvent that the pure azoxy-base separates out. Further supplies of the material will be necessary to decide this point. The crystalline base has no definite melting point, but it begins to shrink at about 200°, and blackens and decomposes at about 223—226°. Attempts were made to acetylate the base by boiling it with acetic anhydride; the substance dissolves at first, but soon separates out again in orange crystals. These, on analysis, proved to be the unaltered compound, the point of decomposition after this treatment being raised to 247°, and the solubility in alcohol and acetic acid being reduced to practically *nil*, either by complete conversion into the insoluble form, or by removal of the last traces of impurity. That the substance was not acetylated was shown by the following result:—

0·0883 gram gave 12 c.c. moist N at 18° C. and 755 2 mm. bar.

	Calculated.	Found.
N	15·73	15·59

We must add that our attempts to acetylate the azoxy-compound were prompted by certain theoretical considerations, which will be discussed later on in this paper. We do not consider that the failure to acetylate under the conditions mentioned can be taken as conclusive proof of the absence of imidic nitrogen.

For comparison with the foregoing results, a specimen of the nitrotriazine was reduced in hot glacial acetic acid by means of zinc-dust. The treatment of the product was the same as before, and the portion insoluble in dilute hydrochloric acid was found to consist of the azoxy-compound, probably mixed with some anhydro-base. The basic portion was likewise submitted to the same treatment as before, our efforts being concentrated upon this substance, in order to obtain further information with respect to the amidotriazine. Some of the base was dissolved in dilute sulphuric acid, diazotised in the cold with sodium nitrite, and the diazo-salt then decomposed by boiling the solution. A regular evolution of nitrogen occurred, but the substance which separated out was resinous and unpurifiable. The fact that the base can be diazotised is good evidence, however, that it contains an amido-group.

Another portion of the base was acetylated by heating with acetic anhydride, but the acetyl derivative did not appear to be more readily purifiable than the base itself. We were more successful with the benzoyl derivative, which was obtained by heating some of the dry base for about 10 minutes with excess of benzoyl chloride. After treating the product repeatedly with hot water, and finally with dilute ammonia, it was dissolved in hot dilute alcohol, and allowed to separate out. The substance was thus obtained as an amorphous, ochreous powder, which was dissolved when dry in boiling toluene, in the hope of obtaining a crystalline product. The compound dissolves with some difficulty in toluene, and separates out on cooling as a very definite deposit, which appears under the microscope to consist of minute, white, spherical aggregates. The aggregates do not appear to be distinctly crystalline, but this nodular, and almost cellular, structure is quite characteristic of the compound. When dry, it forms a white powder, which softens at 171°, and melts with blackening at 176—177°. Analysis showed that this compound was the benzoyl derivative of the amidotriazine:—

0·1036 gram gave 0·2995 gram CO_2 and 0·0481 gram H_2O.
0·1079 „ 11·6 c.c. moist N at 19° C. and 752·3 mm. bar.

	Calculated for $C_{23}H_{16}N_3{\cdot}NH{\cdot}C_7H_5O$.	Found.
C	79·29	78·84
H	4·84	5·15
N	12·33	12·22

A small quantity of the crude base which was left after the preceding experiments was crystallised from toluene, and the first crop of crystalline nodules analysed, with the following result:—

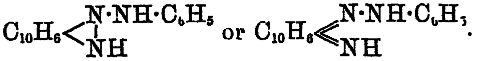
0·0637 gram gave 8·8 c.c. moist N at 16·5° C. and 749·9 mm. bar.

	Calculated for $C_{23}H_{16}N_3\cdot NH_2$.	Found.
N	16·0	15·84

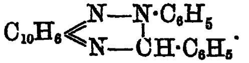
The melting point was the same as that of the former preparation, 190—191°, and we consider that the substance thus isolated is the amidotriazine sought for.

Theoretical Considerations.

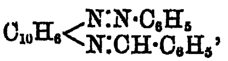
Before discussing the mode in which the triazine ring breaks down under the influence of reducing agents, it is necessary to consider the formula of the triazines generally, as two constitutions have been proposed. The orthoamidoazo-compounds from which the triazines are obtained are regarded by some chemists as hydrazones, *e.g.*, benzeneazo-β-naphthylamine:—


$$C_{10}H_6<\begin{matrix}N\cdot NH\cdot C_6H_5\\ \mid\\ NH\end{matrix} \text{ or } C_{10}H_6\leqslant\begin{matrix}N\cdot NH\cdot C_6H_5\\ NH\end{matrix}.$$

In accordance with this view of the constitution of the orthoamidoazo-compounds, Goldschmidt and Rosell suggest as one formula for the diphenyltriazine,


$$C_{10}H_6\leqslant\begin{matrix}N—N\cdot C_6H_5\\ \mid\\ N—CH\cdot C_6H_5\end{matrix}.$$

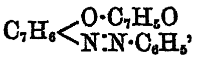
As was pointed out by one of us and F. Hughes in a recent paper (this vol., p. 381), the triazine can also be formed from benzeneazo-benzylidene-β-naphthylamine by simple rearrangement of the bonds. Now this orthoazo-compound cannot be represented as a hydrazone unless we make the very improbable assumption that hydrogen migrates from the carbon atom of the aldehyde residue. The formula of the azo-compound can only be


$$C_{10}H_6<\begin{matrix}N:N\cdot C_6H_5\\ N:CH\cdot C_6H_5\end{matrix},$$

and this and all its analogues are, as might be expected of true azo-compounds, highly-coloured substances. If, therefore, an azo-compound, which cannot possibly be formulated as a hydrazone, passes so readily into a colourless triazine, it seems to us that the quinonoïd formula of the triazines cannot be upheld, and at the same time an additional argument is furnished against the hydrazone formula of the orthoamidoazo-compounds, and, by implication, against the hydrazone formula of the ortho-oxyazo-compounds.

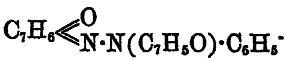
While writing the present paper, another communication by Goldschmidt and Brubacher (*Ber.*, 1891, **24**, 2300) has been published, in which these authors bring forward additional evidence in favour of the hydrazone formula. While admitting the extreme value of the experimental results, we cannot, however, accept these as conclusive. It would be out of place to discuss these results in detail here, as they have but an indirect bearing on the present subject, but we may point out that the reduction of such compounds as the acetate and benzoate of benzeneazo-β-naphthol, and of similar ortho-oxyazo-compounds, appears to us more likely to give rise to the migration of the acid radicle from oxygen to nitrogen than from nitrogen to oxygen. It is not surprising, therefore, that acetanilide and benzanilide should be found among the products of reduction. It is true that these products were not obtained by one of us and G. T. Morgan in the course of an analogous investigation published two years ago (Trans., 1889, **55**, 114), but the difference in the results is no doubt due to our having used stannous chloride and hydrochloric acid, instead of zinc-dust and acetic acid, as a reducing agent. One argument against the hydrazone formula of the orthoazo-compounds is that the hydrazo-compounds obtained by Goldschmidt and Brubachor are apparently non-phenolic.*

Thus, taking as a type the benzoylbenzeneazo-*p*-cresol of these authors, the two formulæ for this compound are:—



$C_7H_6<\begin{array}{l}O\cdot C_7H_5O\\ N{:}N\cdot C_6H_5\end{array}$,

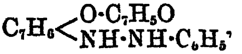
Old formula.



$C_7H_6<\begin{array}{l}O\\ N\cdot N(C_7H_5O)\cdot C_6H_5\end{array}$.

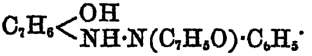
Hydrazone formula.

The hydrazo-compounds would be respectively:—



$C_7H_6<\begin{array}{l}O\cdot C_7H_5O\\ NH\cdot NH\cdot C_6H_5\end{array}$,

I.



$C_7H_6<\begin{array}{l}OH\\ NH\cdot N(C_7H_5O)\cdot C_6H_5\end{array}$.

II.

A compound of formula II might be expected to be phenolic; the fact that it is not so appears, as is indeed admitted by the authors themselves, to give support to formula I, *i.e.*, the old formula which was assigned to the analogous β-naphthyl derivative by one of us and

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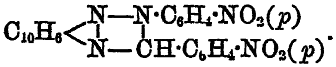
* Another difficulty arising from the adoption of the hydrazone formula is the difference in constitution which must be assigned to the alkyl and alkoyl derivatives of the ortho-azo-compounds. The alkyl radicle is undoubtedly attached to oxygen and not to nitrogen in the former of these compounds (Meldola and Morgan, Trans., 1889, **55**, 603). Goldschmidt and Brubacher explain this by assuming that the salts of these compounds have the true azo-formula $C_6H_5\cdot N_2\cdot C_{10}H_6\cdot OR$. But if the salts have this constitution, their non-phenolic character is still a mystery. If, according to this view, $C_6H_5\cdot NH\cdot N{:}C_{10}H_6{:}O(\beta)$ is transformed into an azo-compound by mere contact with cold alcoholic potash, it may be argued with equal or greater force that $C_6H_5\cdot N_2\cdot C_{10}H_6\cdot OH(\beta)$ is transformed into $C_6H_5\cdot N(C_2H_3O)\cdot N{:}C_{10}H_6{:}O(\beta)$ by prolonged boiling with acetic anhydride.—R. M.

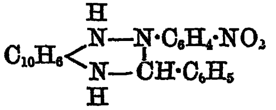
G. T. Morgan in the paper referred to. As a question of constitutional chemistry the problem is, however, a most delicate one, and further investigation will be necessary before we can hope to have it solved. In the meantime, we see no reason for modifying the generally received formula for the orthoazo-compounds, or the corresponding formula for the triazines as used throughout this paper.

The formation of the anhydro-base by the reduction of the ortho- and paranitro-triazines may be best interpreted by an appeal to the results obtained with the metanitrotriazine. The first action of the nascent hydrogen is no doubt the formation of a dihydro-derivative. We have already given evidence of the existence of such a compound in the case of the dinitrotriazine:—



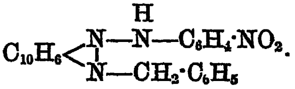
$$C_{10}H_6<\begin{array}{l}N—N\cdot C_6H_4\cdot NO_2(p)\\ |\quad\ \ |\\ N—CH\cdot C_6H_4\cdot NO_2(p)\end{array}.$$

When this compound is boiled in alcoholic solution with zinc-dust and alkali, it becomes decolorised, but immediately reoxidises in contact with the air. Admitting that this result indicates the formation of a very unstable dihydro-derivative, the question then arises as to the position of the hydrogen atoms. In the mononitro-compounds under consideration, two alternatives are possible:—



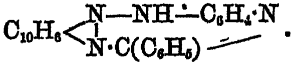
$$C_{10}H_6<\begin{array}{l}\overset{H}{N}—N\cdot C_6H_4\cdot NO_2\\ |\quad\ \ |\\ \underset{H}{N}—CH\cdot C_6H_5\end{array}$$

and



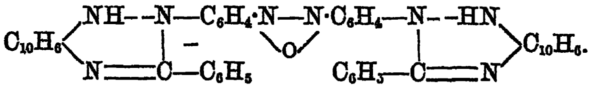
$$C_{10}H_6<\begin{array}{l}\overset{H}{N}—N—C_6H_4\cdot NO_2\\ |\\ N—CH_2\cdot C_6H_5\end{array}.$$

The first of these appears the more probable, as it is more likely that nitrogen would be severed from nitrogen than nitrogen from carbon. Moreover, a nitrodihydro-derivative of the second formula might be expected, under the continued action of hydrogen, to give rise to an anhydro-base by inner condensation:—



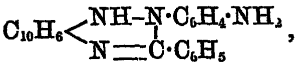
$$C_{10}H_6<\begin{array}{l}N—NH—C_6H_4\cdot N\\ |\\ N\cdot C(C_6H_5)\end{array}.$$

Such a change is highly improbable, and we have never obtained a compound of this kind. The first formula may therefore be accepted, and this contains the group —NH—ÇH—, which is most probably attacked by the oxygen of the nitro-group and converted into the group —N$\equiv$C$\equiv$, the nascent hydrogen at the same time removing part of this oxygen, and 2 mols. coalescing, with the formation of the azoxy-compound:—



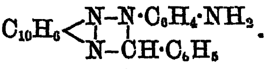
$$C_{10}H_6<\begin{array}{l}NH{-}{-}N—C_6H_4\cdot N—N\cdot C_6H_4—N{-}{-}HN\\ \quad\quad\ |\quad\quad\quad\ \ \diagdown O \diagup \quad\quad\quad\quad |\\ N\!=\!\!=\!C—C_6H_5 \quad\quad\quad C_6H_5—C\!=\!\!=\!N\end{array}>C_{10}H_6.$$

It was this formula which led us to suspect that the azoxy-compound contained imidic hydrogen and to try the action of acetic anhydride upon it as already described. The further action of nascent hydrogen on the azoxy-compound leads to the decomposition indicated by the dotted lines, a portion of this compound breaking down into the anhydro-base and metaphenylenediamine, and another portion into the amidotriazine, which should accordingly have the first, and not the second, of the two formulæ



$$C_{10}H_6<\begin{matrix}NH{-}N{\cdot}C_6H_4{\cdot}NH_2\\ N{=}C{\cdot}C_6H_5\end{matrix},$$

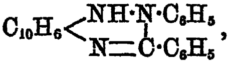
I.



$$C_{10}H_6<\begin{matrix}N{-}N{\cdot}C_6H_4{\cdot}NH_2\\ N{-}CH{\cdot}C_6H_5\end{matrix}.$$

II.

If this interpretation of the formation of the azoxy-compound be correct, the replacement of the NH_2-group by hydrogen by the diazo-reaction should give rise to the compound



$$C_{10}H_6<\begin{matrix}NH{\cdot}N{\cdot}C_6H_5\\ N{=}C{\cdot}C_6H_5\end{matrix},$$

isomeric with diphenylnaphthotriazine. This point will be investigated subsequently. That the azoxy-compound is, in fact, an intermediate product is proved by the circumstance that, when further reduced by boiling the alcoholic solution with zinc-dust and hydrochloric acid, it gives the anhydro-base.

From these considerations, it is legitimate to conclude that the ortho- and paranitro-triazines pass through the same phases on reduction, only the nitro-group appears to be a more energetic oxidiser in these positions, so that the azoxy-stage is passed through more rapidly and the amidotriazine does not appear to be formed. We have good evidence that an azoxy-compound is formed also in the case of these nitrotriazines, and attempts will be made to isolate it. The evidence in question is that if a solution of either of these compounds in cold glacial acetic acid be treated with a small quantity of zinc-dust, insufficient for complete reduction, the solution, which is at first colourless, becomes orange-yellow, and then again colourless if more zinc-dust is added.

The reduction of other nitrotriazines has been studied to some extent, but this part of the work is not yet complete. The products thus far obtained result from the amidation of the nitro-group.

Reduction of the az-p-*Nitrophenyl*-ald-*methyl Derivative.*

We had only a very small quantity of this material to work with, but the results obtained were sufficiently definite. On reduction in alcoholic solution with zinc-dust and hydrochloric acid, a white, crystalline base was obtained, which, after crystallisation from methyl alcohol, formed white needles melting at 173—174°. The substance is somewhat readily oxidised in warm air, with the formation of a reddish colouring matter; for this reason it could not be dried in the water-oven. A specimen was analysed after being allowed to dry in the air at the ordinary temperature for several days:—

0·1131 gram gave 18·3 c.c. moist N at 19·5° C. and 766·3 mm. bar.

	Calculated for $C_{18}H_{14}N_3 \cdot NH_2, \frac{1}{2}CH_4O$.	Found.
N	18·42	18·68

The base crystallises well from dilute ethyl alcohol, and is but slightly soluble in the benzene hydrocarbons. By heating the substance for a few minutes with acetic anhydride, an acetyl derivative was obtained, which was crystallised from dilute alcohol and obtained in the form of white needles which begin to shrink at 156° and fuse at 161—162°.

0·0128 gram gave 1·9 c.c. moist N at 20° C. and 760·7 mm. bar.

	Calculated for $C_{18}H_{14}N_3 \cdot NH \cdot C_2H_3O$.	Found.
N	16·97	16·99

The reduction of the nitrotriazines containing an *ald*-nitro-group gives rise also to the formation of amidotriazines, but these do not appear to be crystallisable, and their examination is not yet concluded. The base obtained in this way from the *as*-phenyl-*ald*-*p*-nitrophenyltriazine is characterised by the intense blue fluorescence which is displayed by its solutions, as well as by the solutions of its salts.

We desire, in conclusion, to express our thanks to the firm of Read Holliday & Sons, Limited, for kindly supplying us with some of the materials used in this investigation, and also to Mr. Julian L. Baker, who assisted us by analysing some of the products described in this paper.

Finsbury Technical College.

LXVI.—*The Action of Picric Chloride on Amines in Presence of Alkali.*

By G. S. Turpin, M.A., D.Sc.

The mobility conferred on a halogen atom which is directly attached to a benzene nucleus by the presence of nitro-groups in the system of atoms is considerably different in kind from that exhibited in the case of halogen derivatives of the paraffinoid hydrocarbons. With the object of determining more fully than had been done by previous workers the particular directions in which the halogen in a typical nitro-derivative tends to react, some experiments were begun by me in the October term of 1888 on the behaviour of picric chloride under various conditions where such bodies as methyl iodide readily react; but before other than negative results had been obtained the work was discontinued, and was only resumed recently, with results some of which are given in this paper.

The negative observations above referred to were made in examining the action of picric chloride on the sodium derivatives of ethyl malonate, and of metallic sodium on the same chloride. A good deal of time was spent over the first of these two reactions, but under no circumstances could any definite product other than sodium picrate be found, a result which is in agreement with the experiments of Dittrich (*Ber.*, **23**, 2725), who has, however, found that with sodium ethylacetoacetate picric chloride reacts in more normal fashion.

The activity of the chlorine in picric chloride seems, then, to lie more especially in the direction of the reactions which replace this chlorine by hydroxyl or by an amido-group (substituted or not), for picramide and similar bodies are obtained from the chloride with about the same readiness as are the picrates. It appeared, therefore, of some interest to ascertain what course the reaction would pursue when picric chloride is exposed to the simultaneous action of an alkali and an amine. It was found on trial that when a solution of two equivalents of sodium hydrate in dilute alcohol is added to the hot alcoholic solution of one equivalent each of the hydrochloride of a primary or secondary amine and of picric chloride, the reaction proceeds very differently according to the character of the amine; that with amines of strongly basic properties an almost quantitative yield of the substituted trinitraniline is obtained, whilst methylaniline and diphenylamine give only sodium picrate; in the case of ammonia itself, the yield of picramide obtained was not good; and the somewhat unexpected observation that the amido-group in sodium sulphanilate reacts readily with picric chloride under the conditions mentioned seems to show that it is not simply a question of the basic power of the amine, but that other influences help to determine the nature of the reaction.

The extreme ease with which picric chloride reacts with amines has often been noticed, and in particular Willgerodt (*J. pr. Chem.* [2], **40**, 264), who has done much valuable work in this field, has noticed that the hydrochlorides of the hydrazines are readily acted on by picric chloride with formation of the corresponding trinitrophenyl derivatives; but, under the conditions above mentioned, the reaction between amines and the chloride occurs so easily, the products being obtained in almost quantitative yield, and in a state of nearly complete purity, that it promises to be of service in obtaining characteristic derivatives of newly prepared amido-compounds. The substituted picramides which have been obtained all crystallise very readily, and are purified by dissolution in alcohol or glacial acetic acid. In applying the reaction, it is, of course, unnecessary to use the hydrochloride of the amine; the base may equally well be employed, but in that case only one equivalent of sodium hydroxide is added.

The following are the individual results obtained on treating various amines with picric chloride and sodium hydroxide in alcoholic solution:—

Ammonia.—2½ grams of picric chloride were dissolved in boiling alcohol, and solutions of 0·54 gram of ammonium chloride and of 0·8 gram sodium hydroxide in dilute alcohol then added. On cooling, a crystalline mass of picramide separated out, which was filtered off and washed first with alcohol and then with water; its weight was 1·4 gram only (60 per cent. of theory), and the melting point of 150—165° showed that the product was far from pure.

Aniline.—In this case the same amount of picric chloride was used, and the corresponding quantity of aniline hydrochloride. It was noticed that a reaction occurred before adding the sodium hydroxide solution. The yield was 2·7 grams of a product melting at 177°, and by recrystallisation from glacial acetic acid this was raised to 177·5°, which is distinctly above the temperature, 175°, given by Clemm (*J. pr. Chem.* [2], **1**, 160) for this substance, trinitrodiphenylamine, or picroaniline, $C_6H_2(NO_2)_3\cdot NH\cdot C_6H_5$.

Septdecylamine.—1·35 grams of septdecylamine hydrochloride (*Ber.*, **21**, 2486) (from stearic acid) treated with the theoretical quantities of picric chloride and sodium hydrate in alcoholic solution gave an immediate precipitate of yellow, crystalline plates, which amounted to about 2 grams. The product was recrystallised from alcohol, in which it dissolves with difficulty, and was obtained in golden-yellow, lustrous plates of the constant melting point 86°.

Picroseptdecylamine, $C_6H_2(NO_2)_3\cdot NH\cdot C_{17}H_{35}$, is soluble in ether readily in benzene, with difficulty in alcohol. When heated on platinum foil, it melts, and then decomposes with slight violence, leaving a bulky, carbonaceous residue.

0·2132 gram gave 21·45 c.c. moist nitrogen measured at 9° C. and 763 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3{\cdot}NH{\cdot}C_{17}H_{35}$.
N	12·15	12·02

Picroseptdecylamine, like the similar derivatives of other primary amines, possesses feeble acid properties; it is insoluble in acids, but slightly soluble in cold potash with a pale yellow colour.

α-Naphthylamine.—In this case the free base was used, and from 1·4 grams of it with 2·5 grams of picric chloride and 0·4 gram of sodium hydrate were obtained 2·55 grams of the expected product. This separated out at once as a red, crystalline solid, which, after being boiled with alcohol, in which it is almost insoluble, melted at 196°. By recrystallisation from glacial acetic acid, the compound was obtained in deep-red, lustrous plates melting at 197°, which are slightly soluble in alkalis, insoluble in acids.

0·2693 gram picro-α-napthylamine gave 38·05 c.c. moist nitrogen measured at 22° C. and 756 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3{\cdot}NH{\cdot}C_{10}H_7$.
N	15·93	15·82

Piperidine.—Here too the base, not the hydrochloride, was employed, and from 0·85 gram of it 2·5 grams of picropiperidine melting at 105·5° were obtained. By further recrystallisation from alcohol, the substance was obtained in orange-red pyramids, which were grown together to form very long, deeply striated needles, and the melting point was raised to 106°. Picropiperidine is insoluble in both acids and alkalis in the cold, except on long standing, or on boiling, when partial decomposition seems to occur.

0·2928 gram substance gave 49·1 c.c. moist nitrogen measured at 19·5° C. and 757 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3{\cdot}NC_5H_{10}$.
N	19·15	18·92

Methylaniline.—It was not found possible by acting with picric chloride on methylaniline, whether alone or in presence of alkali, to obtain any crystalline product except, in the latter case, sodium picrate; in presence of sodium acetate, however, the two substances react partly in the desired direction, though here, too, the chief product is the picrate. 5 grams of picric chloride were dissolved in boiling alcohol, and solutions of 2·15 grams of methylaniline and 3 grams of crystallised sodium acetate were added; the liquid at once acquired a strong odour of acetic acid, and, on cooling, sodium picrate separated out in the characteristic yellow needles, which were filtered off, and found to dissolve almost entirely in water, leaving a very small amount of resin. The alcoholic mother liquor, on standing, deposited a red, crystalline powder, whose quantity was increased by cautious addition of water; this was collected and recrystallised from alcohol, when about half a gram of deep-red, striated plates with a brilliant lustre was obtained. Picromethylaniline, as a nitrogen determination indicated the substance to be, melts at 108°, and is insoluble in both acids and alkalis.

0·1670 gram of the substance gave 26·4 c.c. moist nitrogen measured at 22·5° C. and 754·5 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3 \cdot NCH_3C_6H_5$.
N	17·73	17·61

Diphenylamine behaved in exactly the same way as methylaniline. By treatment with picric chloride in presence of sodium acetate, a small yield of picrodiphenylamine was obtained. The substance crystallises from alcohol in soft, deep-red plates with a fatty lustre, which melt at 62°.

0·2258 gram gave 28·3 c.c. moist nitrogen measured at 9·5° C. and 765·5 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3 \cdot N(C_6H_5)_2$.
N	15·15	14·74

Sulphanilic acid, or, rather, its sodium salt, reacts readily, but the yield obtained is not more than 60 per cent. The acid is dissolved in alcohol, to which a solution of two molecular proportions of sodium hydroxide in water has been added, and the theoretical quantity of picric chloride dissolved in boiling alcohol is mixed with the hot solution of sodium sulphanilate; yellow crystals almost immediately separate out, and their quantity gradually increases as the liquid cools; they are filtered off and recrystallised from water, in which they are very readily soluble, when orange-yellow, lustrous plates are obtained, which from the method of formation and the results of analysis appear to be sodium parapicramidosulphonate,

$$C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_4 \cdot SO_3Na + 2\tfrac{1}{2}H_2O.$$

The salt is almost insoluble in absolute alcohol, but very readily soluble in water. Heated on platinum foil, the substance decomposes without melting, and leaves a very bulky, carbonaceous residue. The acid has not yet been isolated, but it is intended to continue the examination of this compound as well as of the action of picric chloride on other amidosulphonic acids. The water of crystallisation was driven off at 140°, and the amount found corresponds most nearly to the presence of 2½ mols. of water.

3·3554 grams of the salt, dried between filter paper, lost 0·3308 gram when heated at 140° and finally at 155°.

	Found.	Calculated for $2\frac{1}{2}H_2O$.
H_2O	9·86 p. c.	9·98 p. c.

The anhydrous salt absorbs moisture very rapidly from the air, and appears to be more soluble in water than the hydrated salt, for when stirred on a watch glass with a very small quantity of water, it dissolves to a clear solution, which presently becomes almost solid from the separation of yellow, crystalline plates.

The following results were obtained in the analysis of the dried substance:—

0·2582 gram gave 0·0469 gram Na_2SO_4.
0·3197 „ 0·1751 „ $BaSO_4$.

	Found.	Calculated.
Na	5·89	5·67
S................	7·57	7·88

Amidophenol.—One of the first substances that was subjected to treatment with picric chloride was orthamidophenol, but it was soon found that in this case the reaction does not follow the normal course, or at least does not stop at the formation of picramidophenol. With the corresponding para-derivative, on the other hand, the action proceeds regularly, and it will therefore be better to take the case of the para-isomeride first.

Paramidophenol.—The reaction proceeds regularly, and a good yield is obtained whether the base or its hydrochloride is treated with the theoretical quantities of picric chloride and sodium hydroxide in hot alcoholic solution. On cooling, the liquid becomes thick from the separation of beautiful, bronze-coloured plates, which, on recrystallisation from alcohol, give dark, purple-brown needles containing one molecule of alcohol of crystallisation. This is given off very slowly over H_2SO_4 even *in vacuo*, but rapidly at 100°, and the crystals are thereby converted into a brick-red mass which, when recrystallised from water or, better, from dilute alcohol, gives scarlet needles free from alcohol. If strong alcohol be taken as the solvent, the original purple-brown needles are obtained.

I. 0·8034 gram of the crystals from alcohol dried over H_2SO_4 lost 0·0976 gram when heated at 100°.

II. 0·6548 gram lost 0·0811 gram when similarly treated.

	Found. I.	Found. II.	Calculated for one molecule C_2H_6O.
C_2H_6O	12·15	12·38	12·57

The analysis of the scarlet needles got by crystallisation from dilute alcohol gave results in agreement with the expected substance, parapicramidophenol, $C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4\cdot OH$.

I. 0·2138 gram gave 0·3503 gram CO_2 and 0·0517 gram H_2O.

II. 0·2446 „ 36·3 c.c. nitrogen at 11° and 764 mm.

	Found.	Calculated.
C..............	44·69	44·39
H..............	2·68	2·50
N..............	17·78	17·51

The molecular weight of the dried compound was determined by Raoult's method, using naphthalene as solvent.

0·5345 gram lowered the freezing point of 40 grams of $C_{10}H_8$ from 4·093° (arbitrary scale) to 3·798°; this gives, taking 70 as the value of the constant for $C_{10}H_8$, M = 316; the calculated number is 320.

Parapicramidophenol melts at 174°; it is slightly soluble in water, readily in alcohol, from which it crystallises in the above-mentioned purple needles containing one molecule of alcohol. The basic character of the parent amidophenol is totally destroyed by the introduction of the strongly negative picryl group, and the picramidophenol possesses well-marked acid properties; it dissolves in alkalis with a very dark-red colour, but is not more soluble in dilute acids than in water itself. On boiling the alkaline solution, decomposition slowly takes place, while the colour becomes less bright, and a slight precipitate is formed.

Acetic anhydride acts readily on parapicramidophenol when boiled with it for a short time; the resulting liquid shaken with water gave a red solid soluble with difficulty in alcohol, but readily in acetic acid, from which it crystallises in dark-red, lustrous prisms melting at 165°. The acetyl derivative is only very slightly soluble in alkalis, showing that it is the hydroxyl group which has been attacked.

0·2089 gram gave 28·8 c.c. nitrogen at 15·5° and 748 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4\cdot OCOCH_3$.
N..............	15·85	15·47

The benzoyl derivative was easily obtained by applying the method of Schotten-Baumann. 2 grams of parapicramidophenol were dissolved in 500 c.c. of dilute soda, and an excess of benzoyl chloride added in successive small portions with vigorous shaking; the solid product was recrystallised from acetic acid, and was thus obtained in orange needles melting at 191° C. The compound is almost insoluble in alkalis.

0·2421 gram gave 27·2 c.c. nitrogen at 17° and 763 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3\,NH{\cdot}C_6H_4{\cdot}OCOC_6H$,.
N	13·09	13·20

The methyl derivative was prepared by boiling the picramidophenol in methyl alcohol solution with rather more than the theoretical quantity of sodium methylate and methyl iodide. The crystals which separated out were filtered off, washed with dilute soda until the filtrate was nearly colourless, then with water, and were finally recrystallised from a mixture of alcohol and acetic acid. Deep-red, silky needles were obtained, which melted at 165° C.

0·2154 gram gave 31·6 c.c. nitrogen at 11·5° and 751 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3{\cdot}NH{\cdot}C_6H_4{\cdot}OCH_3$.
N	17·24	16·77

The compound is soluble with difficulty in alcohol, readily in glacial acetic acid.

Orthopicramidophenol cannot be obtained by acting on orthamidophenol or its hydrochloride with picric chloride and alkali. The product then formed is described on a subsequent page. Neither could a satisfactory yield of pure substance be got by heating the base with picric chloride alone or in alcoholic solution, though in the latter case a small amount of a product was formed which appeared from its reactions to be the impure picramidophenol. Better results followed when orthamidophenol was treated in boiling benzene solution with picric chloride; two molecules of the amidophenol were taken to one of the chloride, and the mixture heated with benzene on the water-bath for two hours. Amidophenol hydrochloride, together with a red substance, separated out as a bulky precipitate, which was filtered off and washed with water to remove the hydrochloride. The residue can be recrystallised from alcohol, best after addition of a few drops of dilute acid, and gives silky needles which are free from alcohol, and are somewhat more crimson in tint than the para-isomeride; they melt at 175° and decompose at 177°, whereas the isomeride does not decompose below 250°. In analysing the substance, it was found necessary to mix it very thoroughly with powdered copper oxide, a precaution which is to be recommended for all picro-derivatives, as otherwise the carbon is found too high and the nitrogen too low, in consequence of the formation of nitrous fumes during the combustion.

I. 0·1826 gram gave 0·2946 gram CO_2 and 0·0447 gram H_2O.
II. 0·2177 „ 33·25 c.c. nitrogen at 18° C. and 762 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_4 \cdot OH$.
C............	44·01	44·39
H	2·72	2·50
N	17·66	17·51

The molecular weight was determined by Raoult's method, with the following result:—

0·4690 gram lowered the freezing point of 40 grams of naphthalene from 4·216° to 3·955°, that is, by 0·261° C.

	Found.	Calculated.
M................	315	320

Orthopicramidophenol dissolves slightly in water, readily in alcohol. It is soluble in alkalis with a dark-red colour; but on allowing the alkaline solution to stand, or immediately on boiling it, a change takes place which results in the formation of the body obtained by treating orthamidophenol with picric chloride and sodium hydroxide in the manner used throughout this work. The change is rendered evident when the alkaline solution is an ammoniacal one by the formation of a precipitate and the decolorisation of the solution. When the liquid contains soda or potash, the change on boiling is shown by the colour becoming a magnificent blue, which is best seen in very dilute solution; this blue disappears as cooling takes place, and a dark-brown substance separates out in microscopic needles, which redissolve if the liquid be boiled again with production of the same blue colour. The transformation of orthopicramidophenol into this substance, which is insoluble in ammonia and in cold solutions of sodium or potassium hydroxide, but dissolves with a blue colour in the latter liquids when heated, takes place with great readiness; in one case, when the air of the laboratory contained a noticeable amount of ammonia, a small specimen of orthopicramidophenol was almost entirely transformed during a single recrystallisation from alcohol, and it is advisable to acidify slightly the liquid used for purifying the picramidophenol.

It has been mentioned that the ortho-isomeride is much more easily decomposed by heat than the parapicramidophenol, and this difference is also evident in the behaviour towards acetic anhydride, which at its boiling point acts regularly on the para-isomeride with formation of an acetyl derivative, while the ortho-compound is completely decomposed with an abundant evolution of nitrous fumes. The orthoacetyl derivative was, however, obtained by the action of excess of acetic anhydride at the ordinary temperature for several days, finally heating on the water-bath for a few hours. The product, after two recrystallisations from glacial acetic acid, forms brown-red, crystalline plates which are almost insoluble in cold potash, but dissolve readily on heating the liquid with production of a red solution, whose colour soon changes to a dirty brown and finally becomes deep blue. The substance melts at 161°, and a nitrogen determination gave results agreeing with the formation of a monacetyl-derivative.

0·2248 gram substance gave 30·96 c.c. nitrogen at 13° and 747 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3{\cdot}NH{\cdot}C_6H_4{\cdot}OCOOCH_3$.
N	15·98	15·47

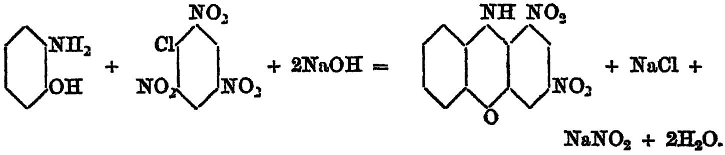
The benzoyl-derivative was prepared by the method of Schotten-Baumann, and the yield obtained was very good when care was taken to work quickly in order to avoid transformation of the orthopicramidophenol by the alkaline solution. The product was recrystallised from glacial acetic acid, and gave orange needles which melt at 191°. Towards alkalis, its behaviour is similar to that of the acetyl compound.

0·2421 gram gave 27·20 c.c. nitrogen at 17° and 763 mm.

	Found.	Calculated for $C_6H_2(NO_2)_3{\cdot}NH{\cdot}C_6H_4{\cdot}OCOC_6H_5$.
N	13·09	13·20

The Action of Alkalis on Orthopicramidophenol.—This action has been already mentioned, but the substance formed in it is best obtained by the direct action of alkali on orthamidophenol and picric chloride in alcoholic solution. Equal molecular proportions of the amidophenol or its hydrochloride and of picric chloride are dissolved separately in boiling alcohol; when the solutions have cooled slightly, they are mixed, and two (or three, if the hydrochloride has been used) molecular proportions of sodium hydroxide dissolved in dilute alcohol are gradually but rapidly added while stirring constantly. The liquid becomes almost pasty from the separation of brown needles, and a noticeable evolution of nitrogen occurs, which continues for a long time and indicates a bye-reaction. It is well, therefore, to filter off the precipitate immediately, using a Witt filtering plate to ensure rapid filtration. The solid product is washed with alcohol and then with water. Its weight is rather less than that of the picric chloride taken, the yield being about 70 per cent. of that theoretically indicated by the explanation of the process which is given below.

If the alcoholic filtrate from this product be evaporated on the water-bath, and the residue extracted with a small quantity of cold water, the solution obtained will be found to contain a large amount of sodium nitrite. On addition of an acid, a very distinct evolution of nitrous fumes occurs, and even when very largely diluted the liquid gives an intense blue when acetic acid is added after potassium iodide and starch paste. Sodium chloride is also present in the solution, and the water used for washing the precipitate was found to contain both chloride and nitrite. The observation that sodium nitrite was produced in the reaction at once threw light on the nature of the process, which is represented by the equation



According to this view, the compound formed is a dinitrophenazoxine, and the results of the analyses which had already been made were found to agree with the composition of such a substance. The product can be purified by crystallisation from benzene or glacial acetic acid, from both of which it is obtained in splendid purple-brown needles which melt at 213°.

I. 0·1992 gram gave 0·3819 gram CO_2 and 0·0501 gram H_2O.
II. 0·1569 „ 0·3050 „ 0·0419 „
III. 0·2054 „ 26·65 c.c. nitrogen at 9° C. and 764 mm.
IV. 0·1801 „ 22·70 „ at 8° C. and 767 mm.
V. 0·2631 „ 32·30 „ at 9° C. and 770 mm.

	Found.					Calculated for
	I.	II.	III.	IV.	V.	$C_6H_4\genfrac{<}{>}{0pt}{}{NH}{O}C_6H_2(NO_2)_2$.
C....	52·28	53·01	—	—	—	52·75
H...	2·79	2·97	—	—	—	2·56
N...	—	—	15·69	15·37	14·98	15·37

(In combustion V the substance was *not* mixed with powdered copper oxide.)

The molecular weight was determined by Raoult's method in naphthalene solution with results which are rather below the theoretical number.

I. 0·2802 gram lowered the freezing point of 40 grams $C_{10}H_8$ by 0·198° C.

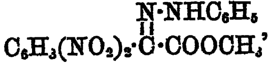
II. 0·2022 gram added to the first solution lowered the freezing point by further 0·140° C

	Found.		Calculated.
	I.	II	
M	246	252	273

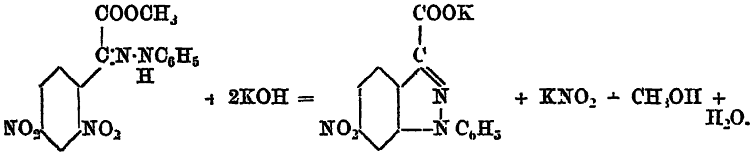
This dinitrophenazoxine is insoluble in water and dilute acids. In potash or soda, but not in ammonia, it dissolves on heating, with a deep blue colour, but separates out unchanged when the liquid cools. Alcoholic ammonia dissolves it in the cold with the production of the same blue colour. In alcohol itself, the substance is practically insoluble, whilst benzene and glacial acetic acid dissolve it very sparingly in the cold, but more readily at their boiling points, and these solutions are deep red in colour. The feeble acid properties of the body are to be attributed to the presence of an imido-group associated with strongly negative groups of atoms, as shown in the formula given above; but the intensity of the red-brown colour of the compound is remarkable in face of the fact that Bernthsen (*Ber.*, **20**, 943) has obtained a pale-yellow substance by the direct nitration of phenazoxine. Further experiments will be made with a view to the confirmation of the constitution which is here attributed to the compound.

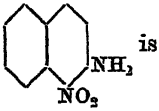
Towards heat, the substance is very stable, melting at 213°, and subliming apparently without decomposition when carefully heated on platinum foil. If quickly heated, it decomposes with slight violence, and leaves a residue of carbon. The hydrogen of the imido-group is not readily replaced by acetyl. Acetic anhydride at its boiling point is without action, and when the two substances are heated to higher temperatures in sealed tubes, more or less of the compound appears to be carbonised and the rest to be unaltered. It can be reduced by treatment with tin and a mixture of acetic and hydrochloric acids, and also appears to form a nitroso-derivative when treated with nitrous acid. These reactions, with others, will be further investigated, and the results given in a subsequent paper.

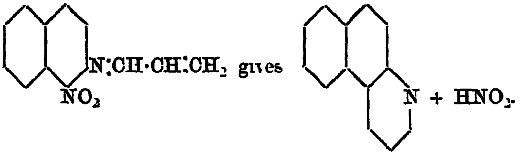
The behaviour of orthopicramidophenol towards alkalis is similar to that observed by Victor Meyer (*Ber.*, **22**, 319) in the case of the compound



$\overset{N\cdot NHC_6H_5}{\overset{\|}{C_6H_3(NO_2)_2\cdot C\cdot COOCH_3}}$, which is easily affected by alkalis according to the equation



The parallelism between the two reactions is very complete. Both can take place in very dilute solution, and in each case the change is made evident by a marked alteration of colour. There is also some analogy with the reaction, previously noticed by Lellmann and Schmidt (*Ber.*, **20**, 3154), which occurs when the nitronaphthylamine  is treated according to Skraup's method for the preparation of quinolines:—



Probably many other picro-derivatives will be found to suffer similar condensation to that described in the case of orthopicramidophenol when treated with alkalis. By acting on α-amido-β-naphthol with picric chloride and sodium hydrate, a substance has been obtained very similar to that formed from orthamidophenol, and it is intended to subject to the same treatment various other compounds which may be expected to give condensation products.

University College, Cardiff.

LXVII.—*Researches on the Terpenes.* II. *On Turpentine.*

By J. E. Marsh and J. A. Gardner.

We give in this paper an account of some experiments illustrating the nature and cause of a remarkable change which ordinary spirit of turpentine undergoes on keeping, whereby its rotatory power becomes considerably increased: we also give some observations on the striking decrease of rotatory power as the boiling point of turpentine rises: we have, further, some remarks to make as to the action of hydrogen chloride on turpentine and the nature of the products formed: and we have finally to notice a striking instance of isomeric change, namely, that under the influence of heat the solid turpentine hydrochloride becomes converted into the isomeric hydrochloride of camphene.

Increase of Rotatory Power of Turpentine on keeping.

A specimen of australene,[*] which had been distilled, gave a rotation of +19° 40′,[†] and readily furnished, when treated with hydrogen chloride, crystals of the solid hydrochloride. After standing some months in a Winchester bottle, its rotation was found to have increased to +21° 10′, and it now gave no crystals when hydrogen chloride was passed into it. After standing five months longer, the rotation was found to have remained constant at +21°. The turpentine was now distilled and the distillate collected in fractions of about equal quantity. The rotation values were taken the same day, and are given in the following table:—

Fraction.	B. p.	Rotation.
I	to 160°	+28°
II	160	+28
III	160	+28
IV	160—165°	+28
V	165—167	+25
VI	167—176	+21

On further keeping the fractions, they did not show an increased, but, if anything, a slightly diminished, rotation after 3½ months.

Terebentene appears to show a similar increase of rotation, but we have studied it less completely, and the increase is much smaller.

In order to determine the cause of the increase of rotation, we subjected several specimens of australene to varied conditions: some were kept in the dark, others exposed to light; of these again, some were exposed to the action of air, dry and moist, others sealed in glass tubes. It will be seen from the table below that only those subjected to the action of moist air, together with exposure to light, showed an increase of rotatory power.

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[*] We retain the original nomenclature of Berthelot, viz., "australene" and "terebentene" for English and French turpentine respectively. If we do not wish to discriminate between them, we use the name "turpentine" simply.

[†] The rotation values are given throughout this paper, except when otherwise stated, for a two-decimeter column of liquid and sodium light.

Change of Rotation of Australene.

Turpentine.	Boiling point.	Initial rotation.	Interval.	Final rotation.
a	161—163°	8° 46′ at 11° C.	75 days	8° 30′ at 18·5° C.
b	161—163	8 46 „ 11 „	„	11 15 „ 19° C.
c	155—157	25 38 „ 11 „	„	25 40 „ 19 „
d	155—157	25 38 „ 11 „	„	26 40 „ 19 „
e	155—157	25 38 „ 11 „	„	25 30 „ 19 „
f	155—157	25 38 „ 11 „	„	25 30 „ 19·5° C.
g	155—157	25 38 „ 11 „	69 days	25 30 „ 19·5 „
h	159—161	13 0 „ 11 „	60 „	13 0 „ 15° C.
i	159—161	13 0 „ 11 „	60 „	16 0 „ 13 „

Of the above specimens, *a*, *g*, and *h* were sealed in tubes and exposed to light; *c* was exposed to light in contact with dry air; *e* was exposed to moist air, and *f* to dry air, both in the dark; whilst those which show an increase of rotation, *b*, *d*, and *i*, were exposed to light in contact with moist air.

We are thus able to convert a turpentine of low rotation into one of the highest possible (?), viz., +28°,* by mere exposure for some weeks to moist air and subsequent rectification.

Decrease of Rotatory Power as the Boiling Point rises.

The observation that the rotation of turpentine decreases as the boiling point rises is, we believe, not new; but we have no remembrance of any definite values being given. The table of boiling points and rotation values for australene, on p. 726, clearly illustrates the fact. A similar table is given below for terebentene, the fractions also being collected in about equal quantity. The decrease is here more regular.

Fraction.	Boiling point.	Rotation.
I	156 —160·5°	−67°
II	160·5—161°	−66
III	161 —162	−65
IV	162°	−65
V	164—167°	−64
VI	164—167	−61
VII	167—180	−57

Still more strikingly is this decrease shown in the case of a specimen of australene where the fractions were not taken in equal quantity, but at equal intervals of temperature.

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* This value is only approximate; later experiments have given 30° 16′ at 18° C.: Landolt gives for pure australene 25° 45′ at 21° C.

Fraction.	Boiling point.	Rotation.
I	155—157°	+24° 56′
II	157—159	+19 36
III	159—161	+13 0
IV	161—163	+ 8 46
V	163—165	+ 2 10
VI	165—167	
VII	167—169	

An analysis made of the mixed fractions V, VI, and VII showed that they still had essentially the composition expressed by the formula $C_{10}H_{16}$.

	Found.	Calculated for $C_{10}H_{16}$.
Carbon	87·1	88·2
Hydrogen	11·8	11·7

Action of Hydrogen Chloride on Turpentine.

Hydrogen chloride has, to all outward appearance, exactly the same action on australene as on terebentene, this action resulting in the production, in each case, of a crystalline solid and a liquid hydrochloride. By a closer study of the reaction it is found that there is one essential difference between australene and terebentene, in this respect: that whereas hydrogen chloride decreases the original dextrorotation of australene, it increases the original lævorotation of terebentene. The solid hydrochlorides are perfectly definite crystalline bodies, but differ in the numerical value as well as in the sign of their rotatory power, the specific rotation, $[\alpha]_D$, of australene hydrochloride being only from +3° to +5°, while that of terebentene hydrochloride is as high as −31°. The liquid hydrochloride has always been a puzzle; is it to be regarded as a single substance, a definite isomeride of the solid, or is it a mixture, and, if a mixture, what are the constituents? We should have little to add to the discussion of this matter were it not that Professor Wallach has recently put forward the view that the liquid hydrochloride is a mixture of the crystalline substance with dipentene dihydrochloride. This appears to us to be quite untenable, and on two main grounds: (1) the amount of hydrogen chloride absorbed by turpentine is never greater than the quantity represented by equal molecules, whereas, if the compound $C_{10}H_{16},2HCl$ were formed, a larger quantity of hydrogen chloride would be required; (2) the rotatory power of terebentene hydrochloride (liquid) is greater than that of the original terebentene, whilst that of the australene compound, though less than that of the original australene, is still considerable. These facts, as will be seen later, are inconsistent with Wallach's supposition.

With regard to the first point, experiments have been made on both a large and a small scale, as to the amount of hydrogen chloride which is required to fully saturate a given quantity of turpentine. These point conclusively to an absorption in molecular proportion, $C_{10}H_{16} + HCl$.

I. 300 grams of australene absorbed 80 grams of HCl; calculated for $C_{10}H_{16} + HCl = 80$ grams.

II. 99 grams of terebentene absorbed 25 grams HCl; calculated, 26 grams.

III. 4·91 grams of terebentene absorbed 1·27 grams HCl; calculated, 1·31 grams.

There is thus no evidence here of the formation of a compound $C_{10}H_{16} + 2HCl$.

With regard to the second point, namely, that of rotatory power, we are met with the difficulty of determining the influence of the solvent on the rotation of the active substance dissolved. But we must ascribe an almost miraculous influence to the solvent if we are to accept the view that the liquid hydrochloride of turpentine is a mixture of the solid with dipentene dihydrochloride.

We find, for example, that the liquid hydrochloride from terebentene of rotation $-66°$ has itself a rotation of $-70° 30'$, while that from australene of rotation $+24°$ has a rotation of $+11°$. Let us assume for the moment that we have here a mixture of dipentene dihydrochloride with terebentene and australene hydrochloride respectively: then the former, being inactive, may be regarded as the solvent, the latter as the dissolved active substance. From the formula $[\alpha]_D = \frac{10^4 \times \alpha}{lc}$, taking $[\alpha]_D$ for terebentene hydrochloride $= -32°$, and for australene hydrochloride $= +5°$, we find that, to give the values obtained above, we must have in each case a solution containing at least 110 grams of active substance in 100 c.c. of solution, a manifest absurdity, since the specific gravity of the liquid is very near that of water. We are thus led, both on the ground of quantitative experiments and on the ground of optical activity, to reject Wallach's interpretation of the constitution of the liquid product.

We have endeavoured to determine the nature of the hydrocarbon or hydrocarbons produced by the removal of HCl from the liquid hydrochloride, and we have been able to recognise dipentene among the products obtained from australene, though not from terebentene. We have recognised it by the formation, properties, and analysis of its tetrabromide. Our experiments on this subject are not yet complete, but we noticed further, both in the case of the australene and of the terebentene compound, a marked diminution of rotatory power on the removal of HCl. The production of dipentene in this way from australene does not necessarily imply the pre-existence of dipentene dihydrochloride in the liquid.

Causes which influence the Production of the Crystalline Hydrochloride of Australene.

We have already noticed that the change which australene undergoes when kept, whereby its rotation is increased, is associated also with its incapacity to furnish at once, on passing hydrogen chloride, the crystalline australene hydrochloride. We believe the difficulty which is occasionally met with in producing this compound to be due to this cause, and not, as Wallach supposes, to the presence of moisture and to the heating of the liquid. We find, indeed, that the solid in question is readily obtained when the product is allowed to become warm, and even if water is added to it, provided the australene has been freshly distilled. It is, in fact, a disadvantage to cool the liquid by a freezing mixture, or with ice, as it does not absorb the gas so readily; on removing it from the ice-water, the liquid becomes heated, and on again passing hydrogen chloride without cooling, the solid is readily obtained.

Isomeric Change of Turpentine Hydrochloride into Camphene Hydrochloride.

The solid crystalline hydrochloride of turpentine, when heated by itself in a sealed tube to 250°, undergoes an isomeric change, whereby, instead of the original substance, the isomeride camphene hydrochloride is obtained. The camphene was separated from the latter by heating with aniline, distilling in steam, and rectifying; it melted at 50°. We have not yet determined whether the change can be brought about at a lower temperature by the aid of carriers, such as aluminium or ferric chloride. Should this be so, we shall have a ready means of obtaining camphene in large quantity.

University Laboratory,
Oxford.

LXVIII.—*On Diphenylisosuccinic Acid and β-Diphenylpropionic Acid.*

By G. G. Henderson, D.Sc., M.A., F.I.C., Assistant to the Professor of Chemistry, University of Glasgow.

When ethyl sodiomalonate is heated with a solution of bromodiphenylmethane in benzene, sodium bromide separates and *ethyl diphenylisosuccinate* is formed, thus:—

$$CH(C_6H_5)_2Br + CHNa(COOC_2H_5)_2 = CH(C_6H_5)_2 \cdot CH \cdot (COOC_2H_5)_2 + NaBr.$$

Preparation of Bromodiphenylmethane.

Bromodiphenylmethane is easily obtained by the action of bromine on diphenylmethane (Friedel and Balsohn, *Bull. Soc. Chim.*, **33**, 339). Diphenylmethane (1 mol.) is heated to 120—130° in a long-necked flask by means of an oil-bath, and bromine (1 mol.) is added gradually through a dropping funnel. When the evolution of hydrogen bromide has almost ceased, the yellowish-brown liquid is poured into a flat basin, which is left to stand under a bell-jar over soda-lime until fumes are no longer evolved. On cooling, the liquid solidifies to a crystalline mass of bromodiphenylmethane, which is freed from a small quantity of adherent oily matter by pressure between folds of bibulous paper, and is then sufficiently pure for most purposes. It is best obtained in a state of purity by crystallisation from dry light petroleum, in which it is readily soluble. It crystallises in groups of hard, colourless prisms, very easily soluble in benzene and carbon disulphide, but decomposed by alcohol; m. p. 39° (uncorr.). The yield is almost quantitative.

Preparation of Ethyl Diphenylisosuccinate, $CH(C_6H_5)_2 \cdot CH(COOC_2H_5)_2$.

32 grams of ethyl malonate are dissolved in about ten times their volume of dry benzene in a flask attached to a reversed condenser, and 4·6 grams of sodium in fine wire are added; after heating for some time on the water-bath, the reaction is complete. 49·4 grams of bromodiphenylmethane are now added, and the heating is continued for some hours until the liquid has a neutral reaction. The sodium bromide which has been formed is removed by filtration, and the benzene is then distilled off, leaving in the flask an orange-coloured oil. This oil is dissolved in cold alcohol and the solution is left to evaporate spontaneously. As evaporation proceeds, the oil again separates out, but gradually changes into a mass of fine needles,

which are drained with the filter pump and recrystallised from alcohol *Ethyl diphenylisosuccinate* is thus obtained in the form of clusters of small, shining prisms or needles which are readily soluble in alcohol, ether, and benzene, and which melt at 54° (uncorr). Analyses of the ester, dried in the exsiccator over sulphuric acid, gave the following results:—

I. 0·1848 gram substance gave 0·4955 gram CO_2 (= 0·1351 gram C) and 0·1126 gram H_2O (= 0·125 gram H).

II. 0·1947 gram substance gave 0·5230 gram CO_2 (= 0·1427 gram C) and 0·1188 gram H_2O (= 0·0132 gram H).

	Found.		Calculated for
	I.	II.	$C_{20}H_{22}O_4$.
C	73·13	73·30	73·62
H	6·76	6·74	6·74
O	—	—	19·64
			100·00

The yield of the ester is good. It may be noted that bromodiphenylmethane has no action on ethyl sodiomalonate till the temperature is raised to 70—80°, and hence no reaction takes place when ether is used as the solvent.

Preparation of Diphenylisosuccinic Acid, $CH(C_6H_5)_2\cdot CH\cdot(COOH)_2$.

The hydrolysis of the ester is easily effected by heating it on the water-bath with an alcoholic solution of 1½ times the calculated quantity of caustic potash. As soon as the alcohol approaches its boiling point, fine needles of the potassium salt separate out, and, it the solution is concentrated, it appears to solidify almost instantaneously, being completely filled with a mass of small, interlacing crystals. Very little of the salt is left in solution, but on filtering off and heating the filtrate, a small additional quantity is obtained. After being washed with cold alcohol, the salt is dissolved in water, and on acidifying the solution with hydrochloric acid the free *diphenylisosuccinic acid* is precipitated as a mass of very delicate needles. It crystallises from dilute spirit in small, shining, colourless prisms, which are very soluble in alcohol and fairly soluble in hot water, but almost insoluble in cold water; it melts with decomposition at 173° (uncorr.). Analyses of the acid, dried at 110°, gave the following results:—

I. 0·1946 gram substance gave 0·5047 gram CO_2 (= 0·1380 gram C) and 0·0932 gram H_2O (= 0·0103 gram H).

II. 0·2308 gram substance gave 0·6000 gram CO_2 (= 0·1636 gram C) and 0·1100 gram H_2O (= 0·0122 gram H).

	Found.		Calculated for
	I.	II.	$C_{16}H_{14}O_4$.
C	70·91	70·89	71·11
H	5·29	5·28	5·18
O	—	—	23·71
			100·00

Salts of Diphenylisosuccinic Acid.

The *potassium* salt, $C_{16}H_{12}K_2O_4,2H_2O$, crystallises in delicate, silky needles, very soluble in water, but, as stated above, only very sparingly soluble in alcohol. When heated to 115°, it loses 2 mols. of water of crystallisation; the anhydrous salt is very hygroscopic. An analysis gave the following results:—

0·4693 gram salt gave 0·0450 gram H_2O and 0·2163 gram K_2SO_4 (= 0·0965 gram K).

	Found.	Calculated for $C_{16}H_{12}K_2O_4,2H_2O$.
H_2O	9·60	9·42
K	20·56	20·42

Most of the other salts are insoluble, or only sparingly soluble, in cold water, and can therefore be prepared by addition of solutions of metallic salts to a solution of the potassium salt. The following are the more characteristic:—

The *calcium* salt precipitates slowly in the form of small, colourless crystals, very sparingly soluble in hot water, and the *barium* salt crystallises in stellate groups of delicate, white needles; it is sparingly soluble in hot water. The *magnesium* salt is fairly soluble in cold, and readily in hot, water; it crystallises in radiating clusters of small, colourless prisms. The *cobalt* salt crystallises in tufts of very delicate needles of a light-pink colour; it is sparingly soluble in cold water, but easily soluble in hot water. The *nickel* salt, on the other hand, is almost insoluble in water, and precipitates slowly as a light-green powder.

The *lead* salt is a white, insoluble powder, and the *copper* salt a light-blue, crystalline powder, almost insoluble in water.

The *silver* salt, $C_{16}H_{12}Ag_2O_4$, is obtained as a white powder, insoluble in water and unaltered by light. An analysis gave the following results:—

0·1500 gram substance gave 0·2172 gram CO_2 (= 0·0592 gram C), 0·0375 gram H_2O (= 0·0042 gram H), and 0·0666 gram Ag.

	Found.	Calculated for $C_{16}H_{12}Ag_2O_4$.
C	39·49	39·67
H	2·77	2·48
Ag	44·40	44·62
O	—	13·23
		100·00

With solutions of the potassium salt, ferric salts give a bulky, yellowish-white precipitate, and chromium salts a voluminous, light-green precipitate, soluble on boiling to a dark-green solution.

Preparation of β-Diphenylpropionic Acid, $CH(C_6H_5)_2 \cdot CH_2 \cdot COOH$.

As already stated, when diphenylisosuccinic acid is heated to its melting point it begins to decompose, and when the melted acid is heated to 175—180°, carbon dioxide is given off with brisk effervescence, and *β-diphenylpropionic acid* is formed, thus:—

$$CH(C_6H_5)_2 \cdot CH(COOH)_2 = CH(C_6H_5)_2 \cdot CH_2 \cdot COOH + CO_2.$$

The clear, brownish-coloured liquid solidifies on cooling to a crystalline mass, which dissolves, with effervescence, in hot sodium carbonate solution. On diluting the solution with water, a small quantity of oily matter separates out, but is easily removed by shaking up with a little ether, and the clear solution is then acidified with hydrochloric acid. The precipitated β-diphenylpropionic acid is washed with water and recrystallised from dilute spirit. It crystallises in delicate, colourless needles, easily soluble in alcohol, but very sparingly soluble in water, and melts at 151° (uncorr.). Analyses of the acid, dried at 110°, gave the following results:—

I. 0·1580 gram substance gave 0·4600 gram CO_2 (= 0·1255 gram C) and 0·0904 gram H_2O (= 0·0100 gram H).

II. 0·1736 gram substance gave 0·5054 gram CO_2 (= 0·1378 gram C) and 0·1012 gram H_2O (= 0·0112 gram H).

	Found.		Calculated for $C_{15}H_{14}O_2$.
	I.	II.	
C	79·42	79·39	79·64
H	6·35	6·47	6·19
O	—	—	14·17
			100·00

When heated with lime, the acid, as is to be expected, yields diphenylethane, $CH(C_6H_5)_2 \cdot CH_3$.

Salts of Diphenylpropionic Acid.

Sodium diphenylpropionate, $C_{15}H_{13}NaO_2,4H_2O$, is remarkable for its great solubility in water and in alcohol. It crystallises in small, colourless needles, which, when heated to 110°, lose 4 mols. of water of crystallisation. An analysis of the salt, dried in the air, gave the following results:—

0·8706 gram substance gave 0·1990 gram H_2O and 0·1881 gram Na_2SO_4 (= 0·0609 gram Na).

	Found.	Calculated for $C_{15}H_{13}NaO_2,4H_2O$.
H_2O	22 85	22·50
Na	7·00	7·18

The *calcium* salt crystallises in white needles, readily soluble in hot, but sparingly in cold, water, whilst the *barium* salt is readily soluble in water.

Silver diphenylpropionate, $C_{15}H_{13}AgO_2$, is a white powder, which is insoluble in water and does not darken on exposure to light. An analysis of the salt, dried at 110°, gave the following results:—

0·3440 gram substance gave 0·6794 gram CO_2 (= 0·1853 gram C), 0·1248 gram H_2O (= 0·0138 gram H), and 0·1113 gram Ag.

	Found.	Calculated for $C_{15}H_{13}AgO_2$.
C..............	53·86	54·05
H	4·(3	3 90
Ag	32·35	32·43
O..............	—	9·62
		100·00

The *copper* salt crystallises from hot water, in which it is sparingly soluble, in blue prisms. The *lead* salt is a white, insoluble powder. The *cobalt* salt separates from hot water, in which it dissolves sparingly, in thread-like, pink crystals. The *nickel* salt is a light-green powder, insoluble in water. The *ferric* salt comes down as a bulky yellowish precipitate, which is decomposed by boiling water. The *manganous* salt crystallises in short, whitish-pink prisms, fairly soluble in water.

Ethyl diphenylpropionate, $CH(C_6H_5)_2{\cdot}CH_2{\cdot}COOC_2H_5$, is prepared by suspending the silver salt in a small quantity of alcohol, adding the calculated quantity of ethyl iodide, and heating for some time on the water-bath. The precipitated silver iodide is removed by filtration, and the filtrate is mixed with about an equal volume of ether and left to evaporate spontaneously. Ethyl diphenylpropionate crystallises out in colourless needles, which are easily soluble in alcohol and in ether, and melts at 63° (uncorr.).

An analysis of the ester, dried over sulphuric acid, gave the following results:—

0·1864 gram substance gave 0·5551 gram CO_2 (= 0·1514 gram C) and 0·1211 gram H_2O (= 0 0132 gram H).

	Found.	Calculated for $C_{17}H_{18}O_2$.
C	80·15	80·31
H	7·22	7·09
O	—	12·60
		100·00

Chemical Laboratory,
University of Glasgow.

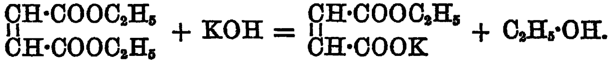
LXIX.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF EDINBURGH UNIVERSITY.

No. III. *Preparation and Properties of Ethyl Hydrogen Fumarate and Ethyl Hydrogen Maleate.*

By JOHN SHIELDS, Ph.D., B.Sc.

Ethyl Hydrogen Fumarate.

THIS acid ethereal salt was first obtained by Laubenheimer (*Annalen*, 88, 294) from impure diethyl fumarate. When a mixture of fumaric acid and alcohol is heated in a sealed tube at 120° until all the acid has disappeared, and the alcoholic liquid then treated with water, diethyl fumarate is precipitated. It was noticed, however, that the impure liquid thus obtained, on standing, deposited a leafy mass of crystals, which had the composition of ethyl hydrogen fumarate. Laubenheimer also succeeded in obtaining a small quantity of this substance in another manner. If gaseous hydrogen chloride is led through an alcoholic solution of malic acid until it is completely saturated, and the mixture afterwards distilled, ethyl hydrogen fumarate is contained in the last portions of the distillate. In this way, Laubenheimer obtained only a very small quantity of ethyl hydrogen fumarate, a quantity totally inadequate for the correct determination of its properties. He therefore attempted to prepare it by the partial hydrolysis of diethyl fumarate, thinking that by employing one-half of the quantity of potash necessary for the complete hydrolysis of diethyl fumarate he would obtain the ethyl potassium salt, according to the equation—



$$\begin{array}{l}CH\cdot COOC_2H_5\\ \|\\ CH\cdot COOC_2H_5\end{array} + KOH = \begin{array}{l}CH\cdot COOC_2H_5\\ \|\\ CH\cdot COOK\end{array} + C_2H_5\cdot OH.$$

The experiment, however, proved unsuccessful. He found that an alcoholic solution of diethyl fumarate, on partial hydrolysis by a concentrated aqueous solution of potash, yielded only dipotassium fumarate, whilst the other half of the ethereal salt remained unattacked. On repeating this experiment and employing a dilute alcoholic, instead of a concentrated aqueous, solution of potash, I obtained large quantities of ethyl potassium fumarate, and from this, by the action of hydrochloric acid, the acid ethereal salt itself. Laubenheimer noticed, on adding the caustic potash to the ethereal salt, that a white, crystalline precipitate was thrown down, which, on analysis, proved to be almost pure dipotassium fumarate, and that from the filtrate from this substance, water precipitated unchanged diethyl fumarate. From these facts alone he concluded that one-half of the ethereal salt underwent complete hydrolysis, whilst the other half remained intact, and does not seem to have actually estimated the amount of unchanged ethereal salt or the quantity of this substance represented by the dipotassium fumarate which he obtained. It is, therefore, not strange that he overlooked the presence of ethyl potassium fumarate in the filtrate, as this salt is excessively soluble in water and dissolves easily in alcohol.

The following method for the preparation of ethyl hydrogen fumarate was found to give very good results. Malic acid was first converted into fumaric acid by heating it in open dishes at a temperature of 140—150°, according to the method recommended by Baeyer (*Ber.*, 18, 676). The unaltered malic acid having been extracted with water, the residue, consisting substantially of fumaric acid, was converted into the diethyl salt in the ordinary way, by dissolving it in alcohol and saturating the solution with gaseous hydrogen chloride. After evaporating off the hydrochloric acid and the excess of alcohol, the diethyl fumarate was "salted out," washed with a dilute solution of ammonium carbonate, dried, and distilled. The pure ethereal salt obtained in this manner was then partially hydrolysed by means of alcoholic potash. For this purpose, 17·5 grams of caustic potash were dissolved in about half a litre of absolute alcohol, and gradually added to a solution of 50 grams of diethyl fumarate in 150 c.c. alcohol, the mixture being vigorously shaken all the time. A white precipitate, amounting to 7·3 grams and consisting of dipotassium fumarate, which is insoluble in alcohol, separated out and was filtered off. The filtrate was evaporated and the residue heated on the steam-bath until all the alcohol was driven off; it was then dissolved in a small quantity of water and 23 grams of unchanged diethyl fumarate extracted with ether. Hydrochloric acid was now added to the aqueous solution and the ethyl hydrogen fumarate extracted with ether, from which, on evaporation, it crystallised in fine, large, four-sided plates. The weight of the acid salt obtained was 16·6 grams. If, now, we calculate the quantity of diethyl fumarate which has been converted into dipotassium and ethyl potassium fumarate respectively, we obtain the following numbers:—

Quantity of diethyl fumarate converted into dipotassium fumarate	6·5	grams
Quantity of diethyl fumarate converted into ethyl potassium fumarate	19 8	„
Quantity of diethyl fumarate unchanged	23 0	„
	49 3	„

Of the 50 grams of diethyl fumarate employed, 49·3 grams, or practically all, are satisfactorily accounted for.

Ethyl hydrogen fumarate is only sparingly soluble in cold, but easily in hot water, and the solution, on cooling, deposits it again in the form of rectangular plates which melt at 70°. It is easily soluble in alcohol and ether. The acid salt, recrystallised from hot water, was analysed, and gave the following results:—

I. 0·1829 gram substance gave 0·0926 gram H_2O and 0·3339 gram CO_2.

II. 0 1825 „ 0·0921 „ 0 3335 „ CO_2.

	Found. I.	Found. II.	Calculated.
C	49·80	49·84 p. c.	50·00 p. c.
H	5·65	5·61 „	5·56 „

Ethyl potassium fumarate is obtained in the form of glistening scales on neutralising ethyl hydrogen fumarate with potassium carbonate, evaporating to dryness, and crystallising from hot absolute alcohol. It is soluble in about its own weight of water at the ordinary temperature; the sodium and ammonium salts are also very soluble in water. These salts are much less, though still easily, soluble in alcohol, and can be precipitated from their alcoholic solutions by the addition of ether, in which they are quite insoluble. The ethyl potassium salt gave the following result on analysis:—

0·2701 gram substance gave 0·1281 gram K_2SO_4.

	Found.	Calculated.
K	21·26 p. c.	21·43 p. c.

A strong aqueous solution of ethyl sodium fumarate gave no precipitate when mixed with the following reagents: calcium chloride, barium chloride, copper acetate, or lead acetate. Silver nitrate, on the other hand, gave a white precipitate of ethyl silver fumarate, soluble in ammonia and in nitric acid, but only sparingly so in cold water; it dissolves easily, however, in hot water, and the solution on cooling deposits the salt again in well-developed crystals. These were dried at 100° and analysed.

0·0930 gram substance gave 0·0400 gram Ag.

	Found.	Calculated.
Ag..........	43·01 p. c.	43·02 p. c.

As ethyl hydrogen fumarate is an unsaturated compound, we should naturally expect it to combine directly with bromine, and give us ethyl hydrogen dibromosuccinate. In order to put this supposition to the test, some of the acid ethereal salt was dissolved in dry chloroform, and a few drops of a solution of bromine in the same solvent added; as the intensity of the colour due to the bromine scarcely diminished on standing a considerable time, the method employed by Kekulé (*Annalen*, Suppl. 1, 131) for the preparation of dibromosuccinic acid was adopted. 3 grams of ethyl hydrogen fumarate, together with a little water and 3·4 grams of bromine, were sealed up in a tube and heated at a temperature of 100° for an hour. On cooling, the brown colour of the bromine had entirely disappeared, and the liquid in the tube consisted of two layers, the lower of which was oily in appearance. This was separated from the upper layer and washed successively with several small portions of water, and then dissolved in ether and dried with chloride of calcium. On evaporating the ether, a colourless oil remained, which crystallised after standing a little. This substance was easily soluble in alcohol, ether, and hot light petroleum; from the last solvent, it was obtained in well-developed crystals which fused at 68°. On analysis, these crystals, presumably ethyl hydrogen dibromosuccinate, gave the following numbers, which agree very well with those theoretically required by the formula of this compound:—

0·1059 gram substance gave 0·1308 gram AgBr.

	Found.	Calculated.
Br..........	52·56 p. c.	52·63 p. c.

0·0338 gram substance required for neutralisation 1·17 c.c. of a 1/9·5 normal baryta solution.

	Found.	Calculated.
Replaceable hydrogen.	0·36 p. c.	0·32 p. c.

Ethyl hydrogen dibromosuccinate is therefore a monobasic acid, as we should expect.

When ethyl hydrogen dibromosuccinate was dissolved in absolute alcohol and the solution saturated with gaseous hydrogen chloride, diethyl dibromosuccinate was formed; it was precipitated from the alcoholic solution on the addition of water, and sometimes solidified during the process of washing. When dissolved in ether and dried with calcium chloride, the ethereal solution, on evaporation, deposited diethyl dibromosuccinate in crystals which melted at 66°. These crystals were analysed without further purification.

0·1222 gram substance gave 0·1397 gram AgBr.

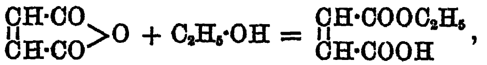
	Found.	Calculated.
Br	48·66 p. c.	48·19 p. c.

The difference between the amount of bromine found and that calculated is probably due to the presence of a small quantity of ethyl hydrogen dibromosuccinate which had not been converted into the diethyl salt by the action of alcohol and hydrogen chloride.

Ethyl Hydrogen Maleate.

For the sake of comparison, the corresponding derivatives of maleïc acid were prepared. Potassium ethyl malonate can be obtained, in a manner similar to that by which its isomeride, potassium ethyl fumarate, is prepared, by the partial hydrolysis of diethyl maleate.

It is preferable, however, to make the ethyl hydrogen salt directly, by the action of alcohol on maleïc anhydride, thus:—



$$\begin{matrix}\text{CH}\cdot\text{CO}\\ \| \\ \text{CH}\cdot\text{CO}\end{matrix}\!\!>\!\text{O} + C_2H_5\cdot\text{OH} = \begin{matrix}\text{CH}\cdot\text{COOC}_2\text{H}_5\\ \| \\ \text{CH}\cdot\text{COOH}\end{matrix},$$

and then to neutralise with potassium carbonate. The maleïc anhydride which I employed in this experiment was prepared by distilling malic acid with acetyl chloride, according to the method recommended by Perkin (*Ber.*, **14**, 2547) and by Anschütz (*Ber.*, **14**, 2791). The anhydride melting at 53° was mixed with an excess of absolute alcohol and heated for a short time on the steam-bath; dry potassium carbonate was then added to the liquid until it was completely neutralised. On cooling, the liquid solidified to a mass of leafy crystals of potassium ethyl maleate. In order to separate this substance from the excess of potassium carbonate, and from a little dipotassium maleate which is formed at the same time, it was placed in an extracting apparatus and extracted with hot absolute alcohol. After evaporating off the alcohol on the steam-bath, the potassium ethyl maleate was still found to be contaminated with diethyl maleate. This impurity was removed by taking advantage of the fact that the potassium ethyl salt is insoluble in ether, whilst the diethyl salt is very easily soluble. The residue, after extracting with ether, consisted of pure potassium ethyl maleate, and was crystallised from hot alcohol. This salt presented the appearance of glistening scales, which exactly resembled those of potassium ethyl fumarate. Like the latter, too, it is very soluble in water, and the sodium and ammonium salts share the same property. On analysis it gave the following result:—

0 1786 gram substance gave 0·0856 gram K_2SO_4.

	Found.	Calculated.
K	21·49 p. c.	21·43 p. c.

A solution of ammonium ethyl maleate, prepared by neutralising the acid with ammonia, gave a white precipitate of silver ethyl maleate on the addition of silver nitrate. The precipitate was soluble in ammonia and in nitric acid, soluble also in hot water, from which it crystallised out on cooling. Calcium chloride, barium chloride, and copper acetate gave no precipitate.

Ethyl hydrogen maleate was obtained from the pure potassium salt by decomposing it with dilute hydrochloric acid and extracting with ether. On the addition of the hydrochloric acid, the ethyl hydrogen maleate did not separate out in the form of an oil or precipitate, as was the case when potassium ethyl fumarate was decomposed in the same manner. This is owing to the great ease with which the acid is dissolved by water. In this respect, ethyl hydrogen maleate is comparable with maleic acid itself, which is quite easily soluble in water, whereas fumaric acid and its corresponding derivative are sparingly soluble. The ethereal solution of the acid ethereal salt was agitated with water, in order to remove traces of potassium chloride, and then dried with calcium chloride and evaporated. A colourless liquid was thus obtained, which would not solidify on standing in a vacuum desiccator or in a freezing mixture of ice and salt.

0·2143 gram substance gave 0·3900 gram CO_2 and 0·1069 gram H_2O.

	Found.	Calculated.
C	49·63 p. c.	50·00 p. c.
H	5·54 „	5·56 „

The difference between ethyl hydrogen fumarate and ethyl hydrogen maleate is strikingly shown in the dissociation constants, which Dr. James Walker had the kindness to determine for me. They are—

	K.
Ethyl hydrogen fumarate	0·0475
Ethyl hydrogen maleate............	0·110

Another important difference between ethyl hydrogen fumarate and ethyl hydrogen maleate was observed in their behaviour towards bromine. When ethyl hydrogen maleate was treated in the same way as the isomeric fumarate, most of the bromine disappeared at once, and the liquid became quite hot. After being exposed to the rays of the sun for a short time, the colour of the liquid was light-yellow; every trace of this colour, however, disappeared on warming the mixture in a tightly-corked tube on the water-bath. The lower oily layer was treated with hot light petroleum when a small quantity of it dissolved and crystallised out on cooling; the fusing point of these crystals was 67°, and their other properties agreed exactly with those of the ethyl hydrogen dibromosuccinate (m. p. 68°) which was obtained from ethyl hydrogen fumarate. On analysis:—

0·1120 gram substance gave 0·1382 gram AgBr.

	Found.	Calculated.
Br............	52·50 p. c.	52·63 p. c.

When the bromine was added very slowly to the solution of ethyl hydrogen maleate in water, and the action allowed to go on in the cold, only a trace of the ethyl hydrogen dibromosuccinate melting at 67° was obtained. The syrupy residue, insoluble in light petroleum, was yellowish and very unstable, the slightest rise in temperature being accompanied by an evolution of hydrogen bromide. It is easily soluble in alcohol and ether. It could not be obtained in the solid form by cooling in a freezing mixture.

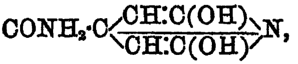
The action of bromine on ethyl hydrogen maleate is quite analogous to its action on maleïc acid. Petri (*Annalen*, **195**, 59) found that bromine not only combines quickly with maleïc acid, even in the cold, forming isodibromosuccinic acid, but that a part of the maleïc acid is at the same time converted into fumaric acid. With ethyl hydrogen maleate, a precisely similar reaction takes place; one portion of it is converted into ethyl hydrogen fumarate, which combines with the bromine, forming the crystals of ethyl hydrogen dibromosuccinate, which were found to melt at 67°, whilst the other, and by far the larger, portion combines directly with the bromine to form the syrupy, unstable liquid, which is, in all probability, ethyl hydrogen isodibromosuccinate. We must, however, be particularly careful not to jump at conclusions, for it would seem, from the experiments of Claus (*Ber.*, **15**, 1844), that a third modification of ethyl hydrogen dibromosuccinate exists, which melts at 275°. Whether this substance is, or is not, what Claus believed it to be remains yet to be proved, but it should be kept in mind that a considerable amount of uncertainty must exist as to the constitution of a substance obtained, as this one was, as a bye-product in the preparation of diethyl dibromosuccinate.

LXX.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XX. *Action of Ammonia on Ethereal Salts of Organic Acids.*

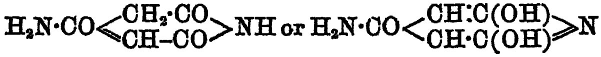
By S. Ruhemann, Ph.D., M.A., University Lecturer in Organic Chemistry, and R. S. Morrell, B.A., late Scholar of Caius College.

Some time ago, one of us published the results of an investigation (Trans., 1887, **51**, 403, *Ber.*, **20**, 799, 3366) on the action of ammonia on ethyl acetylcitrate and on ethyl aconitate, which showed that in this way both the ethereal salts were transformed into a pyridine derivative, the amide of citrazinic acid. This led to the conclusion that the constitution of this compound may be represented by the structural formula



$$\mathrm{CONH_2{\cdot}C}\Big\langle\begin{array}{l}\mathrm{CH{:}C(OH)}\\ \mathrm{CH{:}C(OH)}\end{array}\Big\rangle\mathrm{N},$$

and therefore that the formula of pyridine should be expressed by the symbol suggested by Riedel. The view expressed by Lovén (*Ber.*, **22**, 3053) that the formation of citrazinamide from ethyl acetylcitrate and from ethyl aconitate may be explained just as well if citrazinamide is represented by the formula

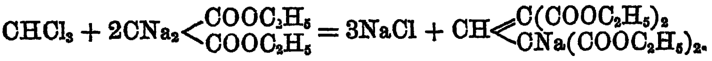


$$\mathrm{H_2N{\cdot}CO}\Big\langle\begin{array}{l}\mathrm{CH_2{\cdot}CO}\\ \mathrm{CH{-}CO}\end{array}\Big\rangle\mathrm{NH} \text{ or } \mathrm{H_2N{\cdot}CO}\Big\langle\begin{array}{l}\mathrm{CH{:}C(OH)}\\ \mathrm{CH{\cdot}C(OH)}\end{array}\Big\rangle\mathrm{N}$$

was found to be incorrect (*Ber.*, **23**, 831).

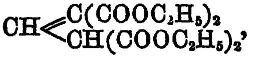
The readiness with which ethyl aconitate is transformed into a derivative of pyridine induced us to investigate the action of ammonia on ethereal salts of acids which have a constitution analogous to that of aconitic acid; and for this purpose we chose glutaconic acid and dicarboxyglutaconic acid, which Conrad and Guthzeit obtained in the course of their interesting researches on syntheses by means of ethyl malonate (*Annalen*, **222**, 249).

Sodium ethylmalonate when acted on by chloroform yields the ethyl salt of sodium dicarboxyglutaconic acid, according to the equation



$$CHCl_3 + 2CNa_2{<}\begin{matrix}COOC_2H_5\\COOC_2H_5\end{matrix} = 3NaCl + CH{<}\begin{matrix}C(COOC_2H_5)_2\\CNa(COOC_2H_5)_2\end{matrix}.$$

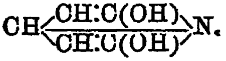
This sodium compound, when warmed with dilute hydrochloric acid, gives the ethyl salt of dicarboxyglutaconic acid,



$$CH{<}\begin{matrix}C(COOC_2H_5)_2\\CH(COOC_2H_5)_2\end{matrix},$$

and this, by the further action of hydrochloric acid, or by heating with sodium hydroxide solution, decomposes with elimination of carbonic anhydride, yielding glutaconic acid, $CH{<}\begin{matrix}CH{\cdot}COOH\\CH_2{\cdot}COOH\end{matrix}$.

This glutaconic acid is closely related to aconitic acid, for aconitic acid may be regarded as carboxyglutaconic acid, so it was to be hoped that ethyl glutaconate would, under the influence of aqueous ammonia, condense in a similar manner and yield *αα'*-dihydroxypyridine,



$CH{<}\begin{matrix}CH{:}C(OH)\\CH{:}C(OH)\end{matrix}{>}N.$

Ethyl Glutaconate.—Glutaconic acid was prepared according to Conrad and Guthzeit's directions by heating the ethyl salt of dicarboxyglutaconic acid with hydrochloric acid, and extracting the solution with ether. The ethereal salt cannot be obtained by passing hydrogen chloride through an alcoholic solution of the acid, as the etherification is accompanied by an addition of hydrogen chloride. On distillation, hydrogen chloride is given off, but the distillate always contains chlorine even after repeated fractionation.

The pure ethereal salt, however, is easily obtained on heating the solution of the acid in absolute alcohol with sulphuric acid on the water-bath; the oil which separates on adding the product to water, after shaking with dilute sodium carbonate solution and drying over calcium chloride, boils at 236—238°. The ethereal salt gave on analysis numbers agreeing with the formula $CH{<}\begin{matrix}HC{\cdot}COOC_2H_5\\CH_2{\cdot}COOC_2H_5\end{matrix}$.

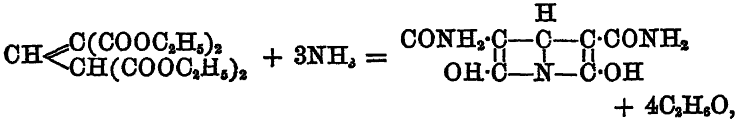
	Calculated for $C_9H_{14}O_4$.	Found.
C	58·06	58·02
H	7·53	7·64

Action of Ammonia on Ethyl Glutaconate.

Ethyl glutaconate, when allowed to stand with aqueous ammonia in a stoppered bottle, dissolves after several days, and the green solution remains clear even after several weeks. Hydrochloric acid gives no precipitate, but the acid solution on exposure to the air deposits after some time a green precipitate, which is soluble in ammonia, and can be thrown down from this solution unchanged on the addition of a mineral acid. The substance thus formed is very soluble in water, but could not be obtained in a state fit for further investigation. It is probable that by the action of ammonia on ethyl glutaconate dihydroxypyridine is first formed, which, however, in solution is readily oxidised by the oxygen of the air.

Action of Ammonia on the Ethereal Salt of Dicarboxyglutaconic Acid.

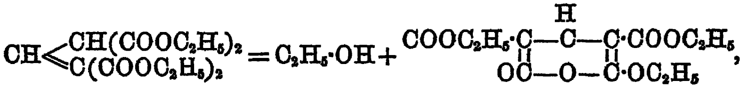
As the expected pyridine derivative from glutaconic acid could not be isolated, we directed our attention to the study of the action of ammonia on the ethyl salt of dicarboxyglutaconic acid, in hopes that the reaction would take place according to the equation



$$\mathrm{CH}{<}\begin{matrix}\mathrm{C(COOC_2H_5)_2}\\ \mathrm{CH(COOC_2H_5)_2}\end{matrix} + 3\mathrm{NH_3} = \begin{matrix} & & \mathrm{H} & & \\ \mathrm{CONH_2{\cdot}C} & - & \mathrm{C} & - & \mathrm{C{\cdot}CONH_2}\\ \| & & | & & \| \\ \mathrm{OH{\cdot}C} & - & \mathrm{N} & - & \mathrm{C{\cdot}OH}\end{matrix} + 4\mathrm{C_2H_6O},$$

and yield the diamide of dihydroxydinicotinic acid. To this view we were, moreover, led by the recent researches of Guthzeit and Dressel (*Annalen*, **262**, 89) on the ethyl salt of dicarboxyglutaconic acid.

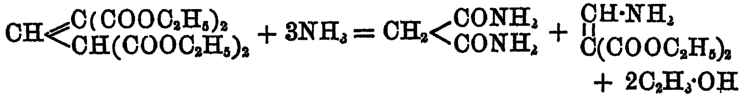
These chemists showed that this ethereal salt splits up according to the equation



$$\mathrm{CH}{<}\begin{matrix}\mathrm{CH(COOC_2H_5)_2}\\ \mathrm{C(COOC_2H_5)_2}\end{matrix} = \mathrm{C_2H_5{\cdot}OH} + \begin{matrix} & & \mathrm{H} & & \\ \mathrm{COOC_2H_5{\cdot}C} & - & \mathrm{C} & - & \mathrm{C{\cdot}COOC_2H_5}\\ \| & & & & \| \\ \mathrm{OC} & - & \mathrm{O} & - & \mathrm{C{\cdot}OC_2H_5}\end{matrix},$$

and that the latter product is readily transformed into a pyridine derivative.

Ammonia acts on the ethereal salt according to the above equation, but the formation of the pyridine derivative seems to be dependent on the concentration of the ammonia. Under the conditions of our experiments only a very small quantity of the etheral salt condenses with ammonia to the amide of dihydroxydinicotinic acid, the greater portion spliting up under the influence of this reagent according to the equation



$$\mathrm{CH}{<}\begin{array}{l}\mathrm{C(COOC_2H_5)_2}\\\mathrm{CH(COOC_2H_5)_2}\end{array} + 3\mathrm{NH_3} = \mathrm{CH_2}{<}\begin{array}{l}\mathrm{CONH_2}\\\mathrm{CONH_2}\end{array} + \begin{array}{l}\mathrm{CH{\cdot}NH_2}\\\|\\\mathrm{C(COOC_2H_5)_2}\end{array} + 2\mathrm{C_2H_5{\cdot}OH}$$

into malonamide and the ethyl salt of amidoethylenedicarboxylic acid.

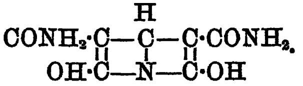
On pouring strong aqueous ammonia on to the ethyl salt of dicarboxyglutaconic acid, a yellow, gelatinous precipitate is at once formed, which is, no doubt, the ammonium compound of the ethereal salt. This disappears in the course of a few days, and the yellow solution remains clear for some time. After the lapse of about a fortnight, colourless crystals separate, which gradually increase in quantity. These crystals are a mixture of malonamide and the ethereal salt of amidoethylenedicarboxylic acid, whilst the ammoniacal solution contains, besides these two compounds, a small quantity of the amide of dihydroxydinicotinic acid. The separation of the three compounds formed in this reaction did not present any difficulty, for malonamide, although readily soluble in water, is insoluble in absolute alcohol, whilst the ethereal salt of the amido-acid is very easily taken up by alcohol, and the pyridine compound dissolves in ammonia, and is precipitated from the ammoniacal solution by hydrochloric acid.

The crystals which had been formed in the action of ammonia on ethyl dicarboxyglutaconate were warmed with absolute alcohol, whereby the ethyl salt of the amido-acid was dissolved, and the malonamide left behind. On distilling off the alcohol, the ethyl amidoethylenedicarboxylate remained as an oil, which solidified on cooling. The ammoniacal filtrate from the crystals darkened on concentration, and deposited slightly coloured needles, which were found to be the diamide of dihydroxydinicotinic acid. The filtrate contained malonamide, mixed with the ethereal salt of the amidodicarboxylic acid, and their separation was effected as mentioned above. Instead of proceeding in this manner, it was found to be more convenient to remove the ammonia as far as possible by passing a current of air through the solution, whereby some of the amido-ether was precipitated; the filtrate was then shaken with ether, which takes up the rest of the ethereal salt of the amido-acid, and the aqueous solution on concentration deposits first the pyridine derivative and then malonamide.

The condensation product formed in this reaction crystallised from water in colourless needles, which gradually became pink, and decomposed without melting at a temperature above 300°. Its composition was fixed by a nitrogen determination, which gave the following numbers:—

	Calculated for $C_7H_7N_3O_4$.	Found.
N	21·32	21·55

The formation of this compound from the ethereal salt of dicarboxyglutaconic acid may be explained in a similar manner to that of citrazinamide from ethyl aconitate, and its constitution may accordingly be represented by the following formula:—



$$\begin{array}{c} \qquad\quad H \\ CONH_2{\cdot}\underset{\|}{C}—\underset{|}{C}—\underset{\|}{C}{\cdot}CONH_2. \\ OH{\cdot}C—N—C{\cdot}OH \end{array}$$

The diamide of dihydroxydinicotinic acid, like citrazinamide, possesses strongly acid properties; it is soluble in ammonia and other alkalis, and is precipitated from these solutions by hydrochloric acid. We were prevented from further investigating this compound on account of the small quantity of substance formed in this reaction, for, as stated before, strong aqueous ammonia transforms almost the whole of the ethyl salt of dicarboxyglutaconic acid into malonamide and the ethereal salt of amidoethylenedicarboxylic acid.

Ethyl Amidoethylenedicarboxylate.

This substance, isolated in the manner described above, is readily soluble in water, especially on boiling, and on cooling an oil separates, which solidifies after a short time. In a vacuum, over sulphuric acid, it crystallises from the aqueous solution in colourless prisms which melt at 66°, and are very soluble in alcohol and ether. On analysis, the following numbers were obtained, which correspond with the formula $NH_2{\cdot}CH{:}C(COOC_2H_5)_2$:—

	Theory for $C_8H_{13}NO_4$.	Found.				
		I.	II.	III.	IV.	V.
C	51·33	51·75	51·43	—	—	—
H	6·95	6·89	6·80	—	—	—
N	7·48	—	—	7·50	7·55	7·58

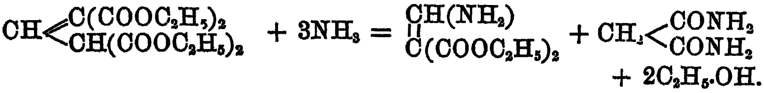
The amido-ether on boiling with an alkali evolves ammonia, reduces mercurous nitrate, and gives a red coloration with ferric chloride; platinic chloride in a concentrated aqueous solution of the compound produces a yellow, crystalline precipitate, which, however, is nothing but ammonium platinochloride.

The third of the substances formed by the action of ammonia on the ethyl salt of dicarboxyglutaconic acid is malonamide. This was proved by its melting point, which was found to be 171° [Freund

(*Ber.*, 17, 133) found 170°], by comparison with a specimen prepared from ethyl malonate, and by the following analysis :—

	Theory for $C_3H_6N_2O_2$.	Found. I.	II.	III.
C	35·30	35·80	—	—
H..........	5·88	6·10	—	—
N	27·45	—	27·21	27·27

The transformation which the derivative of glutaconic acid undergoes under the influence of ammonia takes place for the most part according to the equation



$$CH<\begin{matrix}C(COOC_2H_5)_2\\CH(COOC_2H_5)_2\end{matrix} + 3NH_3 = \begin{matrix}CH(NH_2)\\ \| \\ C(COOC_2H_5)_2\end{matrix} + CH_2<\begin{matrix}CONH_2\\CONH_2\end{matrix} + 2C_2H_5{\cdot}OH.$$

The ethereal salt of amidoethylenedicarboxylic acid seems in this reaction not to be converted into the amide.

Action of Ammonia on Ethyl Benzyldicarboxyglutaconate.

The formation of the ethyl salt of amidoethylenedicarboxylic acid induced us to investigate the behaviour of ammonia towards the ethereal salt of a derivative of dicarboxyglutaconic acid in order to determine if this reagent effects an analogous decomposition in this case also. We chose the benzyl derivative, which, according to Conrad and Guthzeit (*loc. cit.*), is readily obtained by heating the sodium ethyldicarboxyglutaconate with benzyl chloride. The ethyl salt of benzyldicarboxyglutaconic acid,

$$(COOC_2H_5)_2C{:}CH{\cdot}C(COOC_2H_5)_2{\cdot}CH_2{\cdot}C_6H_5,$$

on the addition of strong, aqueous ammonia, first enters into solution, and subsequently an oil separates out, which disappears again after some hours, giving place to crystals which are soluble in hot water, and form colourless needles melting at 225°.

This compound was found to be identical with the benzylmalonamide obtained by Bischoff and Siebert (*Annalen*, 239, 96) from the ethyl salt of benzylmalonic acid and ammonia. It was identified by its properties and the following analysis, the formula for $C_6H_5{\cdot}CH_2{\cdot}CH(CONH_2)_2$ requiring

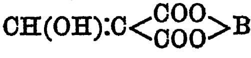
	Theory for $C_{10}H_{12}N_2O_2$.	Found. I.	II.	III.
C	62·5	62·45	62·54	—
H.......	6·25	6·27	6·26	—
N	14·58	—	—	14·61

The ammoniacal filtrate from the crystals which had separated out in the reaction, was freed as far possible from ammonia by a current of air, and then shaken with ether. On distilling off the ether, an oil was left which solidified on cooling, and crystallised from hot water in prisms melting at 66°. This compound is the ethyl salt of amidoethylenedicarboxylic acid, as was further shown by the following nitrogen determination:—

	Calculated for $C_8H_{13}NO_4$.	Found.
N	7·48	7·59

Ammonia, therefore, with the benzyl derivative, also effects a decomposition, yielding benzylmalonamide and the ethyl salt of amidoethylenedicarboxylic acid.

Action of Baryta on the Ethereal Salt of Amidoethylenedicarboxylic Acid.

The ethereal salt, when boiled with baryta, evolved ammonia, and yielded, besides a small quantity of barium carbonate, the barium salt of hydroxyethylenedicarboxylic acid. On heating an aqueous solution of the ethyl salt of the amido-acid with baryta in the proportions of 1 mol. of the first to 2 mols. of the latter, the clear solution became turbid, and a white precipitate was thrown down. This was collected as soon as ammonia ceased to be evolved, and then extracted with boiling water, whereby a small quantity of barium carbonate remained undissolved. Both filtrates, which were neutral to litmus paper, on concentration deposited the barium salt of the organic acid as a white, fibrous mass of needles. This salt, though soluble in water with difficulty, does not easily separate out again from the solution. Instead of evaporating the aqueous solution, the barium salt may be precipitated from it by the addition of alcohol; dried at 100° it has the composition  $CH(OH){:}C{<}\genfrac{}{}{0pt}{}{COO}{COO}{>}Ba$, as indicated by the following barium determination:—

	Calculated for $C_4H_2O_5Ba$.	Found.
Ba	51·31	51·68

We intend to attempt the isolation of the free acid, and hope to communicate the results to the Society in a future paper.

LXXI.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XXI. *Contributions to the Knowledge of Mucic Acid.*

By S. Ruhemann, Ph.D., M.A., and S. F. Dufton, B.A., B.Sc.

Part V.—*Muconic Acid.*

In our previous investigation (this vol., p. 26), we attempted, by the action of phosphorus pentachloride on mucic acid, to prepare tetrachloradipic acid, with the view of replacing, if possible, the halogen atoms by hydroxyl groups, and thus producing a tetrahydroxyadipic acid, probably different from mucic acid. We found, however, that in this reaction phosphodichloromuconic acid is formed at first, and then converted at a higher temperature into Bode's dichloromuconic acid.

We have, therefore, tried to attain the same end starting from tetrabromadipic acid, already described by Rupe (*Annalen*, **256**, 26). Muconic acid is, as stated in a previous paper (Trans., 1890, **57**, 370), prepared from α-dichloromuconic acid by first reducing it to hydromuconic acid by means of tin and hydrochloric acid; the hydromuconic acid thus formed is treated with bromine in glacial acetic acid solution, and the resulting dibromadipic acid subjected to the action of potash. For this last stage Rupe uses alcoholic potash; we find it preferable simply to add the dibrominated acid to a cold strong aqueous solution of potash, and to precipitate the muconic acid by the addition of hydrochloric acid.

Muconic acid, as stated by Rupe, combines directly with 4 atoms of bromine, forming tetrabromadipic acid. Following his directions, we did not succeed, however, in obtaining the acid, even after allowing the mixture of muconic acid and bromine to stand for several days; it is possible that he worked in strong sunlight, which might explain the difference in the results. Nevertheless, it is quite easy to obtain tetrabromadipic acid, even on a large scale, by heating dry muconic acid and bromine on a water-bath in a long-necked flask, the neck forming the internal tube of a condenser; we always noticed in this reaction, which is complete in about 15 hours, an evolution of some hydrogen bromide and the formation of a small quantity of an oil of irritating odour. The product is agitated with ether, which takes up the tetrabromadipic acid, leaving traces of unchanged muconic acid, the ethereal solution is evaporated, and the residue crystallised from dilute alcohol, using animal charcoal to effect complete decolorisation.

The acid thus obtained crystallises in colourless, shining plates, and is identical with that described by Rupe. Its composition was, moreover, verified by a bromine determination, which gave

	Calculated for $C_6H_6Br_4O_4$.	Found.
Br..................	69·3	69·2

Tetrabromadipic acid is almost insoluble in water, but dissolves in ammonia and dilute alkalis, being precipitated unchanged on the addition of mineral acids. Silver nitrate added to a neutral solution of the ammonium salt produces a white precipitate of the silver salt, which, however, slowly decomposes with formation of silver bromide. Though not altered by boiling water, tetrabromadipic acid undergoes change when heated with water in a sealed tube at 120°. On opening the tube, carbonic anhydride escapes; the yellow solution has the smell of burnt sugar and contains some crystals and a small quantity of resinous matter. The filtrate, on concentration, evolves hydrogen bromide and deposits slightly coloured needles which, after recrystallisation from water with use of animal charcoal and drying at 100°, melt at 223° with decomposition. They contain bromine and are soluble in alcohol and in ether. On analysis, they gave numbers corresponding with the formula $C_6H_6Br_2O_6$.

	Theory.	Found.
C	22·63	22·51
H.................	1·89	1·98

The substance is apparently, therefore, the lactone of a dihydroxydibromadipic acid.

Limpricht (*Annalen*, **165**, 271), who previously described tetrabromadipic acid, which, however, does not appear to have been pure, states that it is only slightly attacked by boiling baryta water. We have, on the contrary, found that pure tetrabromadipic acid, although soluble without change in cold baryta water, undergoes a deep-seated decomposition on boiling, a brown precipitate of barium oxalate being thrown down; for, when the latter was decomposed with the required quantity of dilute sulphuric acid, the filtrate, on concentration, deposited long needles which by their properties and analysis were proved to be oxalic acid.

	Theory.	Found.
C	19·0	18·83
H.................	4·76	4·9

The filtrate from the barium oxalate contained an unstable acid, which we did not succeed in isolating.

Alcoholic potash decomposes the acid, on heating, with dark-brown coloration; on evaporating the alcohol, dissolving the residue in water, and acidifying the solution, an acid was liberated; this was soluble in ether, but on evaporating the ethereal solution a resin was left. It is most probable that the acid formed in this reaction is the diacetylenedicarboxylic acid obtained by v. Baeyer from propargylic acid (*Ber.*, **18**, 678).

As we did not succeed in preparing the corresponding hydroxy-acid from the tetrabromo-acid by the action of baryta, potash, or silver oxide and water, it seemed possible that the ethereal salt might give more satisfactory results.

Tetrabromadipic acid cannot be converted into its ethyl salt, either by the action of hydrogen chloride or of sulphuric acid on its alcoholic solution, the acid remaining unchanged in both cases. In order to obtain the ethereal salt of the acid, therefore, we attempted the direct bromination of ethyl muconate, which is easily got by heating the alcoholic solution of muconic acid with sulphuric acid (Trans., 1890, **57**, 374). This ethereal salt was then dissolved in chloroform which had been purified by distillation over calcium chloride, and a solution of dry bromine in chloroform added. We found that 2 atoms of bromine were taken up with considerable readiness, the solution becoming slightly warm; no hydrogen bromide was evolved.

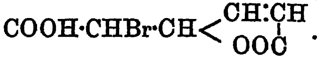
The product is *ethyl dibromhydromuconate*, which is left behind on distilling off the solvent; on recrystallisation from alcohol, it forms beautiful, colourless needles which melt at 84—85°, and are very soluble in ether and chloroform.

The analysis corresponds with the formula

$$COOC_2H_5{\cdot}CHBr{\cdot}CHBr{\cdot}CH{:}CH{\cdot}COOC_2H_5.$$

	Theory.	Found.	
		I.	II.
C	33·51	33·57	—
H............	3·91	3·81	—
Br	44·69	—	44·90

The ethereal salt, when boiled with slightly more than 4 mols. of potash dissolved in alcohol, yields the potassium salt of bromhydroxyhydromuconic acid and potassium bromide. After evaporating the alcohol, the residue is dissolved in water, acidified, and extracted many times with ether, which dissolves the brominated acid. The ether is evaporated and the acid recrystallised from water. On cooling the hot solution, small clusters of needles separate; these decompose at 254° and are very soluble in alcohol. Examination proves this to be the lactone of bromhydroxyhydromuconic acid, the analysis giving results corresponding with the formula



$\mathrm{COOH{\cdot}CHBr{\cdot}CH}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{OOC}\end{matrix}$.

	Theory.	Found.
C	32 58	32·90
H	2 26	2·39

On dissolving the lactone in water, it is transformed again into the corresponding hydroxydicarboxylic acid, since 0·1113 gram required for neutralisation 0 0399 gram of sodium hydroxide, corresponding to 36·13 per cent., whilst the amount calculated for the dicarboxylic acid is 36·2 per cent.

Silver nitrate gives also the silver salt of the dicarboxylic acid as a white precipitate, formed at once on mixing the two solutions.

The formula $\mathrm{COOAg{\cdot}CHBr{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}COOAg}$ requires:—

	Calculated.	Found.
Ag	47 68	47 64

Ethyl Tetrabromadipate.—Although 2 atoms of bromine are very readily taken up by ethyl muconate, the complete bromination of this substance takes place slowly even in direct sunlight. The reaction is best effected, as before, in chloroform solution, and is complete in about two days. After removal of the chloroform, the ethereal salt of tetrabromadipic acid remains as an oil which soon becomes completely solid. Recrystallised from alcohol, it forms colourless, rectangular prisms melting at 70—71°. The formula $\mathrm{COOC_2H_5{\cdot}[CHBr]_4{\cdot}COOC_2H_5}$ was confirmed by a bromine determination, which gave:—

	Calculated.	Found.
Br	61·77	61·40

The further investigation of these compounds in the direction already indicated we hope to complete and lay before the Society in our next communication.

PART VI.—*On the Constitution of Mucic Acid.*

In accordance with the hypothesis of Van't Hoff and Le Bel, two inactive tetrahydroxyadipic acids should exist, unresolvable into active components.

Mucic acid is considered to be one of these possible acids, and we have extended Sohst and Tollens' researches (*Annalen*, **245**, 1) by the preparation and careful examination of the salts which this acid forms with optically active alkaloïds.

Quinine Salt.—Mucic acid is boiled in water with quinine hydrate, and filtered. The filtrate, on cooling, deposits colourless needles, which, after recrystallising from hot water, gave upon analysis:—

	Calculated for $C_6H_{10}O_8,2(C_{20}H_{24}N_2O_2)$.	Found. I.	Found. II.
C	64·32	64·50	—
H	6·76	6·70	—
N	6·53	—	6·86

Cinchonine Salt.—Cinchonine was boiled with mucic acid and water. The solution, filtered and concentrated, deposited clusters of needles, fairly soluble in water, readily in alcohol.

The formula $C_6H_{10}O_8,2C_{19}H_{22}N_2O$ was confirmed by a nitrogen determination—

	Calculated.	Found.
N	7·02	7·09

Strychnine Salt.—Prepared in exactly the same manner as the salts just described, crystallises from water in long needles. The analysis confirmed the formula $C_6H_{10}O_8,2(C_{21}H_{22}N_2O_2)$.

	Calculated.	Found.
N	6·38	6·47

In these three cases, one salt only was formed, and on treatment with a mineral acid the same acid, mucic acid, was reproduced.

Mucic acid is, therefore, undoubtedly one of the unresolvable tetrahydroxyadipic acids.

On heating with water at 170°, unresolvable mesotartaric acid is converted into its resolvable isomeride racemic acid; it seemed to us, therefore, possible that the acid described by Malagouti (*Annalen*, **15**, 179), produced by boiling down the aqueous solution of mucic acid, might bear to this acid the same relationship as racemic acid does to mesotartaric acid. This view was proved by our experiments to be incorrect. Following Malagouti's directions, we extracted the dry residue, obtained by evaporating the aqueous solution of mucic acid with alcohol, but instead of evaporating in a vacuum over sulphuric acid, as Malagouti did, we distilled off the alcohol and recrystallised the solid residue from hot alcohol.

The substance obtained gave on analysis:—

	I.	II.
C.................	38·14	38·21
H.................	5·73	5·59

These numbers prove that the product is not mucic acid or an isomeride, which would require 34·28 per cent. carbon and 4·76 per cent. hydrogen, but that it must be a partially etherified acid. To test this view, we heated the above product with absolute alcohol for several hours on the water-bath; the alcoholic solution on concentration deposited crystals which, dried at 100°, gave on analysis:—

C....................	39·47
H....................	5·93

These numbers agree very closely with those required by the monethyl salt of a tetrahydroxyadipic acid, which would require 40·3 per cent. carbon and 5 88 per cent. hydrogen.

To determine whether this ethereal salt was derived from mucic acid itself or an isomeride, we completed the etherification by passing hydrogen chloride into the alcoholic solution. The resulting diethyl salt was found to be identical in every respect with ordinary ethyl mucate.

These experiments show that Malagouti's paramucic acid cannot be an isomeride of mucic acid. Since, also, mucic acid even when boiled for several hours with alcohol is not changed, whilst the so-called paramucic acid under similar treatment yields the monethyl salt of ordinary mucic acid (as shown by its conversion into ordinary ethyl mucate), we were led to the view that paramucic acid is an anhydride. We were engaged in its further investigation when Emil Fischer (*Ber.*, **24**, 2136) published an account of his experiments on the same subject, and showed that on boiling the aqueous solution of mucic acid it is in part converted into a lactone which he further found to be incompletely etherified on boiling with alcohol.

Although it would seem that Malagouti's paramucic acid is not an isomeride of mucic acid, but the lactone of this acid, E. Fischer (*loc. cit.*) has succeeded in transforming mucic acid into a different tetrahydroxy-acid, allomucic acid, by heating it with pyridine.

LXXII.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XXII. *Orthoquinolinehydrazine.*

By S. F. Dufton, B.A., B.Sc., Assistant Demonstrator in the Cambridge University Chemical Laboratory.

In view of the great importance of hydrazines, both as reagents and in the synthesis of nitrogen compounds, it seemed desirable to prepare and investigate one or more of the possible hydrazines of quinoline, with the special object of determining the influence of the strongly-positive quinoline nucleus on the chemical character of the hydrazine.

Of the three nitroquinolines known, the ortho-compound is the most readily attainable, and this, therefore, I have taken as the starting point of my research.

Orthonitroquinoline.

By direct nitration of pure quinoline with a mixture of fuming nitric acid and strong sulphuric acid, α- and β-dinitroquinoline and ortho- and meta-mononitroquinoline are produced. From this mixture the ortho-compound is easily separated, in accordance with the directions given by Claus and Kramer (*Ber.*, **18**, 1243). 50 grams of quinoline, dissolved in strong nitric acid, are added to 150 c.c. of fuming nitric acid, and 150 c.c. of concentrated sulphuric acid slowly run into the cooled mixture. The whole is then heated in a long-necked, round flask for 10 hours at a temperature of 80°. The reaction is apt to be too violent at first, but afterwards goes perfectly quietly.

The nitrated product is poured into water, and a solution of about 250 grams of caustic soda added slowly, when from the still acid liquid almost the whole of the dinitro- and metanitro-quinolines crystallise out. After a few hours, the liquid is filtered, and an excess of caustic soda added, when the orthonitroquinoline is precipitated. After washing and recrystallising from alcohol, it forms beautiful, long, almost colourless needles. The yield is about 25 grams.

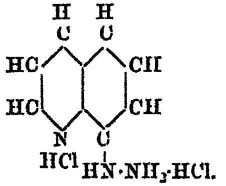
Orthamidoquinoline.

Nitroquinoline is readily reduced to the amido-compound by adding to it the calculated quantity of stannous chloride, both being dissolved in hydrochloric acid. The carefully-cooled mixture, which has become almost solid, is made slightly alkaline with caustic soda, and extracted three times with ether. After drying over potassium carbonate, the ether is evaporated, and the residue distilled in a vacuum; it boils constantly at 271° under a pressure of 20 mm., the distillate being a strongly-refracting, slightly yellow oil which quickly solidifies completely. Claus and Kramer distil the alkaline reduced mixture in a current of steam, but, owing to the considerable solubility of amidoquinoline in water, and to its low vapour pressure at 100°, the method is quite inapplicable to the preparation of large quantities of the substance.

Orthoquinolinehydrazine.

If the amidoquinoline thus prepared be diazotised in the usual way, and the calculated quantity of stannous chloride dissolved in strong hydrochloric acid added, a large, yellow precipitate of a double tin compound of the hydrazine is thrown down. This is collected, washed with strong hydrochloric acid, dissolved in a large quantity of water, and a rapid current of hydrogen sulphide passed through the solution for several hours. After filtering off the tin sulphide, the liquid is boiled down to a small bulk and allowed to crystallise. The crystals thus obtained are dissolved in water, the last traces of tin removed by hydrogen sulphide, and the filtered solution again evaporated. On cooling the concentrated solution, thick, yellow, lustrous prisms of the hydrazine dihydrochloride separate.

Analysis confirms the formula



	Calculated.	Found.		
		I.	II.	III.
C	46·55	46·8	—	—
H	4·74	4·82	—	—
N	18·1	—	18·18	—
Cl	30·6	—	—	30·7

The free hydrazine is best liberated by adding a saturated solution of sodium acetate to the strong aqueous solution of the hydrochloride. The liquid becomes turbid, and extremely fine, long, slightly yellow needles of the hydrazine separate out on standing. After drying in a vacuum over sulphuric acid, they melt at 64°.

Orthoquinolinesemicarbazide.

On mixing aqueous solutions of potassium cyanate and of the hydrazine hydrochloride, a thick, nearly white precipitate is thrown down after a few seconds. This substance, the semicarbazide, when collected, washed with water, and purified by recrystallisation from hot alcohol, forms beautiful white, shining leaflets, which melt at 235° with decomposition.

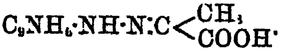
The substance dried in a vacuum over sulphuric acid gave on analysis numbers corresponding to the formula

$$C_9NH_6{\cdot}NH{\cdot}NH{\cdot}CONH_2.$$

	Calculated.	Found. I.	Found. II.
C	59·4	59·34	—
H	4·9	5·01	—
N	27·7	—	27·9

The Pyruvic Acid Hydrazone.

On the addition of pyruvic acid to a strong aqueous solution of the hydrazine hydrochloride, an orange, crystalline precipitate is thrown down. This is the hydrochloride of the pyruvic acid hydrazone, and may be purified by recrystallisation from water, when it forms beautiful orange needles. Sodium acetate liberates the free hydrazone as a light-yellow, insoluble precipitate; washed thoroughly with water, and dried at 100°, it gave on analysis results agreeing with the formula



$$C_9NH_6{\cdot}NH{\cdot}N{:}C{<}{}^{CH_3}_{COOH}.$$

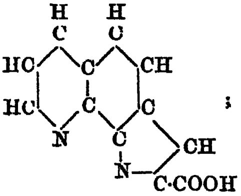
	Calculated for $C_{12}H_{11}N_3O_2$.	Found. I.	Found. II.
C	62·9	63·1	—
H	4·8	4·3	—
N	18·3	—	18·4

The substance melts at 174°, and has both acid and basic properties.

Orthoquinindole-α-carboxylic Acid.

The hydrazones hitherto described, derived from primary hydrazines, do not yield indole derivatives on treatment with concentrated hydrochloric acid, but split up, under the influence of this agent, into the substances used in their formation. The pyruvic acid compound of quinolinehydrazine, however, is readily condensed to an indolecarboxylic acid when heated with hydrochloric acid. It is only necessary to boil the clear solution of the hydrazone in hydrochloric acid for a short time when the liquid becomes filled with yellow crystals of the indolecarboxylic acid. These are filtered, washed with water, and dissolved in a large quantity of boiling alcohol. The hot filtered solution, if diluted with water, deposits slender, colourless needles on cooling: these are very sparingly soluble in water, somewhat more readily in alcohol, and melt at 286° with decomposition.

The formula of the compound is



;

this was verified by analysis, which gave

	Calculated for $C_{13}H_7N_2O_2$.	Found. I.	Found. II.
C............	67·8	67·7	—
H	3·7	3·7	—
N............	13·2	—	13·2

I hope to communicate the results of a further investigation of this hydrazine in a short time.

In conclusion, I must express my hearty thanks to Dr. Ruhemann for the very kind encouragement and advice he has given me during the course of this investigation.

LXXIII.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

No. IV. *Oxidation of Cobalt Salts by Electrolysis.*

By Hugh Marshall, D Sc., F.R.S.E.

Several years ago I contributed a short note on cobalt ammonium alum to the Royal Society of Edinburgh (*Proc. Roy. Soc. Edin.*, **14**, 203). A full report of the work done in connection with the subject has, however, not yet been published. For a considerable time I was unable to carry the research further, and afterwards found some difficulty in repeating the experiments with satisfactory results. During the past year I have again taken up the subject with much greater success, and the results so far obtained are described in the present paper.

My attention was first called to the subject by a peculiar action noticed during the electrolytic separation of copper and cobalt by Claisen's method. The solution which was being analysed contained copper, cobalt, potassium, and hydrogen sulphates, and it was found that if too strong a current was employed to separate the copper, the colour of the solution, notwithstanding the rapid deposition of the metal, did not change to pink, as was expected, but became greyish-green. As this was apparently only slightly, if at all, altered by prolonged action of the current, some of the liquid was removed and tested for copper by means of sulphuretted hydrogen solution. This immediately changed the colour to pink, while the liquid became opalescent through separation of sulphur. There was, however, no copper present. This behaviour pointed to oxidation of the cobalt as the cause of the peculiar appearance, and it was found on testing the remainder of the solution with various reducing agents that these all brought about the change of colour from green to pink.

The next point to be settled was whether the amount of oxidation corresponded to any definite oxide or was only partial. For this purpose, two solutions were made up, one containing the sulphates before mentioned, the other being similar, except that it contained no cobalt. In each case there was a relatively large proportion of copper salt. These solutions were then electrolysed under similar conditions. The solution containing the cobalt behaved as in the case above mentioned. When it was evident that the copper was all precipitated, the current was stopped, and pure ferrous sulphate solution added to each in equal quantity. This changed the colour of the cobalt solution to pink. The two were then titrated back with standard permanganate solution, when, as was expected, the cobalt solution required less than the other, corresponding to the oxidising action of the green compound formed. The amount of extra oxygen thus estimated was sufficient to raise barely one-sixth of the cobaltous salt present into cobaltic. The blank experiment, in which no cobalt was employed, was to get rid, as far as possible, of errors due to the formation of other oxidising agents. The result, whilst proving conclusively that oxidation had taken place, showed that it was only to a comparatively small extent.

From the conditions under which the action took place, it seemed most natural to conclude that the compound formed was a cobaltic salt, but the colour seemed to contradict this view. Solutions obtained by dissolving cobaltic hydrate in cold acids, and supposed to contain cobaltic salts, are brown. The supposition that a double salt might be formed did not seem quite satisfactory. The double sulphates of other similar metals—the alums—have not always the same colour as the simple sulphates which form them, as in the case of iron, but then they do not exist as such in solution in water. It therefore seemed necessary to isolate the substance in the pure state before it would be possible to decide conclusively as to its composition.

The part which the copper sulphate played seemed fairly evident. By its electrolysis we have a powerful oxidising agent—nascent SO_4 ions—liberated without at the same time setting free an equally active reducing agent, the copper being deposited directly as such on the cathode. Some of the SO_4 ions thus liberated would then act upon some of the cobaltous sulphate, converting it directly into cobaltic salt. Assuming the formation of the latter, the reaction might be represented by the equation

$$CuSO_4 + 2CoSO_4 = Cu + Co_2(SO_4)_3.$$

Of course this action is only very partial, large quantities of oxygen being also produced from decomposition of the water in the ordinary way.

The presence of the copper salt was, however, a considerable drawback, and it was sought to effect a similar result by a special form of apparatus. Two ways suggested themselves as suitable: 1st, the electrodes might be placed in separate vessels connected by a tube; or, 2nd, they might be separated from one another by a porous partition. In either case we should expect to see oxidation take place in the liquid surrounding the anode.

The second method was the one adopted. The solution to be oxidised was contained in a beaker, in the centre of which stood a porous battery jar containing dilute sulphuric acid. The anode consisted of a spiral of stout platinum wire placed in the outer cell, while a sheet of copper in the inner one acted as cathode. The solution contained cobalt, potassium, and hydrogen sulphates, the former roughly in the proportion $2CoSO_4 : K_2SO_4$. whilst the latter was in large excess. The current was supplied by two large Bunsen's elements in series, that being the strength employed in the first experiments.

During the passage of the current, the colour gradually changed, becoming first purplish, but next morning it was dark-brown, not at all like the colour of the solutions previously obtained. The current was continued for some time, but little change seemed to occur, and there was no appearance of anything approaching a green colour.

The ratio of extra oxygen to cobalt in the solution was then determined, and this showed that fully a third of the cobalt might exist as cobaltic salt. The ratio would probably be too high, due to the presence of other oxidising agents. The solution behaved exactly like the brown solution obtained by dissolving cobaltic hydrate in sulphuric acid. It decomposed slowly on standing, rapidly if warmed. It was quickly reduced by easily oxidisable substances. Hydrogen peroxide decomposed it with rapid evolution of oxygen; hydrochloric acid with liberation of chlorine. When shaken with pure ether, a green coloration was produced, changing in course of time to pink. A similar effect was produced by very weak alcohol when added in small quantity. Caustic potash gave a black precipitate.

A new experiment was next tried with a modified apparatus. The beaker was replaced by a platinum basin which acted simultaneously as anode. A small porous cell was suspended centrally in this, a spiral of copper wire being employed as the cathode. The cell was filled with solution as before, but a stronger current was used, namely, three cells. The behaviour of the solution was the same as in the previous experiment. By next morning, however, a slight muddy deposit had formed round the side of the basin above the level of the liquid. It was mostly of a brown colour, but there was an edging coloured greenish-blue. On touching the basin, the deposit fell into the liquid and dissolved almost entirely. As the further action of the current produced no change in the appearance of the solution, the experiment was stopped.

Up till now it had been assumed that the potassium sulphate was a necessary constituent of the solution, but it was necessary to prove whether this was so or not. An experiment was therefore started in which simply an acid solution of cobaltous sulphate was electrolysed in the above-described manner. The current was allowed to act all night, and next morning the appearance was quite unchanged. Some ammonia solution was then added so as to form ammonium sulphate with part of the free acid. The current was then continued as before.

The colour now gradually changed, becoming first violet, and next morning the solution was a deep greenish-blue. On pouring off the liquid, some small, dark-blue crystals were found in the bottom of the vessel. These, when examined under the microscope, showed no distinct form, having apparently been largely redissolved. On examining the reaction of the solution, it was found to contain copper, evidently from a brass ring above the basin, which had been attacked by acid spirted on it. A fresh solution was therefore made up in the same manner as before and similarly treated. The behaviour was exactly as before, and in the course of two days a crop of crystals was obtained. These were removed and dried between filter paper. When examined under the microscope, they proved to be nearly all perfect octahedra, whilst a few showed faces of the dodecahedron and the cube. The total quantity weighed about 1 gram, and was all used for analysis. The ammonia determination was unfortunately spoiled. The percentages obtained agreed well for cobalt ammonium alum, considering that it is not possible to get the crystals quite pure and free from mother liquor.

	Found.	Calculated for alum.
Co	12·5	12·1
SO_4	41·2	39·6

The experiment was continued after making up the liquid with more of the original solution, and after several days a quantity of substance amounting to 2 or 3 grams was obtained. The analysis of this gave the following results:—

	Found.	Calculated for alum.
Co	12·70	12·10
NH_4	3·75	3·71
SO_4	39·38	39·62
H_2O by diff.	44·17	44·57

In the next experiment, potassium sulphate was again employed in place of the ammonium salt, and as much as the solution would dissolve was used. The solution behaved precisely as with the ammonium sulphate, becoming deep greenish-blue. The only crystals which separated in the course of several days, however, were potassium sulphate. At last a few dark-blue crystals were noticed among the colourless ones. Some strong solution of cobaltous sulphate was then added and the liquid further electrolysed. In this way a blue deposit was at last obtained, which was freed as much as possible from mother liquor by pressing between filter paper. The soft cake thus obtained, although it necessarily still contained a considerable proportion of impurity, was analysed with the following results:—

Co	10·45
K	9·98
SO_4	51·70
Difference	27·87

It was, therefore, concluded to be a mixture of the alum with potassium hydrogen sulphate.*

Several experiments were next tried with nickel sulphate in place of cobalt sulphate. but without result.

While engaged in these experiments, an abstract of a paper by Kehrmann (*Ber.*, **19**, 3101*b*) appeared in this Journal, describing the preparation of a double cobaltic potassium oxalate which yielded a green solution. In Classen's handbook on quantitative electrolytic analysis, it is stated that during the deposition of cobalt from cobaltous double oxalate solutions the liquid becomes first green and ultimately colourless. It seemed highly probable that this colour was due to the oxidation of the cobalt, according to the equation

$$2CoC_2O_4 + C_2O_4 = Co_2(C_2O_4)_3.$$

This cobaltic oxalate would then unite with the alkaline oxalate present to give the compound obtained by Kehrmann. To confirm this, a solution containing potassium cobaltous oxalate and oxalic acid was electrolysed in the apparatus, as used in the preparation of the alum, when a bright green solution was obtained. This was not reduced by sulphuretted hydrogen in the cold, but on standing some time it gradually changed to a solution of cobaltous salt. Owing to this decomposition and the great dilution, it was not possible to crystallise out the solid salt. There seemed no doubt, however, that a cobaltic compound was actually formed.

As already mentioned, the further study of the subject was not proceeded with for a considerable time, and when again taken up great difficulty was experienced in repeating the experiments, in so far as getting crystals of alum was concerned. The blue solutions could be prepared without much difficulty.

One point which early became evident was the necessity of some means of keeping the temperature of the solution constant, as decomposition sometimes occurred, due to heating caused by the passage of the current for a prolonged period. A coil of glass tube through which cold water circulated was first tried, but without satisfactory results. It appears preferable to cool directly the outside of the basin, as it is in the layer in contact with it that the oxidation takes place. For this purpose a special cooling apparatus was constructed. The arrangement will be understood from the following diagram, which roughly represents a section through the whole apparatus.

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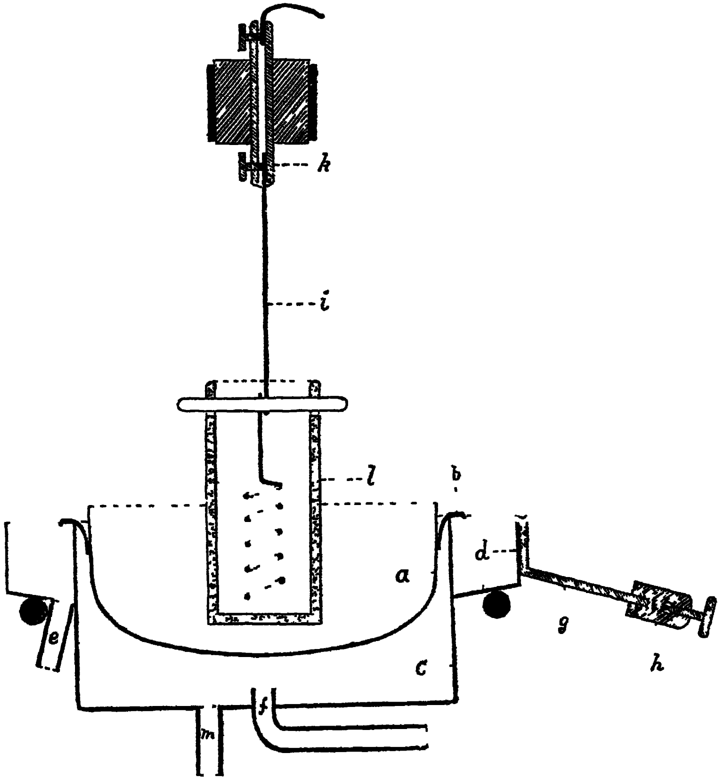
* In all probability it was a mixture of cobaltic sulphate with potassium persulphate.



The platinum basin *a*, of about 200 c.c. capacity, is supported in a copper ring *b*. The latter is made of stiff sheet metal, in which a circular opening, considerably smaller than the basin, is cut. The inner edge of this ring is then cut in to a sufficient depth at short intervals, and the teeth thus formed bent downwards, till the basin can be pushed inside and still held firmly. This ring in turn rests on the edge of the cylindrical vessel *c*, which is also made of copper. It is provided with a trough *d*, to the bottom of which a short outflow tube *e* is attached. In the centre of the bottom of the vessel *c*, is the supply tube *f*. The short arm *g* has a binding screw *h* soldered to it. The whole is supported by the ring of an ordinary retort stand. The cathode consists of a stout platinum wire *i*. This is attached to the tubular binding screw *k*, which passes through an india-rubber stopper held by an ordinary retort stand clamp. This ensures the insulation of the cathode. The porous cell *b* is supported by a small glass rod, which passes through two holes drilled in the sides, and also through a loop on the platinum wire *i*.

The whole cooling apparatus, except where electrical contact is necessary, is coated with black varnish, to preserve the metal from corrosion by acid liquid spirted on it from the basin. Cold water enters by *f*, rises round the basin, and flows over the edge into the trough, escaping at *e*. This continued flow of water keeps the points of contact between the basin and the ring, and between the ring and the vessel *c*, always clean, so that we have complete metallic connection between the basin and the binding screw *h*.

The apparatus acts very efficiently. Even with strong currents, the temperature of the liquid in the basin may be kept within 2—3° of that of the cold water, while that in the inner compartment may be 20—25° higher.

The small tube *m* was added so that the apparatus might be used as a steam bath in electrolytic analysis with warm solutions, as in the estimation of cobalt. The steam is introduced by the tube *f*, and the condensed water escapes at *m*. When used for cooling, the latter opening is of course closed.

The solutions first experimented on were prepared by saturating dilute sulphuric acid (1 acid to 8 water by vol.) with cobalt and potassium or ammonium sulphates. The inner cell was filled with dilute sulphuric acid. During the electrolysis, the liquid in the outer cell of course gets more and more strongly acid. The ordinary porous pots are gradually attacked by the acid, and some aluminium and ferric sulphates get into solution. For this reason it is advisable to use any one pot for only a limited period, and also to use those made from pure kaolin free from iron. The current as a rule varied from 1½ to 2½ ampères, and was supplied from a battery of accumulators, which made the work much less troublesome than when ordinary batteries had to be employed. The solution containing ammonium sulphate was first tried, as it had given the most satisfactory results previously. The liquid became distinctly blue in the space of an hour or two, and after fully two days a solid began to separate. This was finely crystalline, and when agitated gave the liquid a peculiar silky appearance. Examined under the microscope, it was seen to consist of small needles, with here and there a larger piece, somewhat resembling the partly dissolved alum crystals first obtained. When a considerable quantity had separated, forming a muddy deposit on the botom of the basin, it was filtered off through a piece of very thin platinum foil, pierced with numerous fine holes. The foil was laid, just like a piece of filter paper, on the flat perforated plate of a porcelain funnel. The paste thus obtained was then dried in thin layers on porous plates. When dry, it was scraped off, and formed a crystalline, powdery mass, of a fine, blue colour. The analysis gave no satisfactory result. The ratio of cobalt to ammonium was not a simple one, and the amount of sulphuric acid was much in excess of what was required for both metals. A slight excess was of course to be expected, owing to adhering mother liquor, of which the last traces can hardly be removed by the method of drying adopted.

Other products gave similar irregular results on analysis, showing that mixtures were obtained. Experiments were next tried in which potassium sulphate was employed. Here exactly the same thing occurred. The substance obtained had the same appearance and the same irregular composition as in the case of the ammonium compound. As a rule the proportion of alkaline metal was lower than in the alum, which seemed strange, as large quantities were present in the mother liquor. The explanation of this non-formation of alum was at length accidentally discovered. In an experiment with the potassium salt a white, crystalline powder separated first from the blue solution. This was supposed to be potassium sulphate, but was examined and found to be practically free from sulphate. Its properties and the subsequent analysis proved it to be potassium *persulphate.** Taking this formation of persulphate into account, it seemed highly probable that the blue substance was really impure cobaltic sulphate, and an experiment with a saturated solution of cobaltous salt alone in dilute sulphuric acid was started. The solution became blue exactly as in the other cases, and ultimately deposited a similar solid. This was separated and dried as above described, and analysis showed that it was cobaltic sulphate, with a large quantity of water of crystallisation. The following numbers were obtained:—

	Found.	Calculated for $Co_2(SO_4)_3,18H_2O$.
Co	16·0	16·07
SO_4	41·1	39·50
H_2O	43·7	44·43

The water was estimated directly by ignition with lead chromate. The sulphuric acid is in excess, as was to be expected, from the presence of free acid; consequently also part of the oxygen of the free acid is twice reckoned, coming in with the water. Some of the impure specimens first obtained were found to contain considerable quantities of aluminium sulphate from decomposition of the silicate in the porous pot. The quantity of water of crystallisation in the formula noted above was supposed to be probably the most correct. Aluminium sulphate crystallises with 18 mols. H_2O in the hydrate occurring naturally as "hair salt."

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* See succeeding paper, p. 771.

As already mentioned, the substance forms a blue, crystalline powder. When the paste is dried on porous plates, the surface has a silky appearance. If kept in a dry atmosphere, or if gently warmed, it loses water, and rapidly decomposes, becoming first of a brownish colour, which quickly gives place to pink. If kept in a moderately moist atmosphere, this does not take place nearly so readily; some which has been kept in a tightly stoppered tube for months does not show any signs of decomposition. Treated with water, it dissolves, but immediately begins to decompose, becoming of a dark, purplish colour, quickly changing to a greyish, neutral tint, and ultimately becoming pink. The oxygen liberated is evolved briskly during the process. The greyish tint seems to indicate that the colours of the cobaltous and cobaltic salts are nearly complementary. The salt dissolves very easily and without immediate decomposition in dilute sulphuric acid. Such a solution is greenish-blue, but gradually decomposes completely in the course of a day or two. It is, of course, very easily decomposed by all reducing agents. It gives a black precipitate when alkali is quickly added. The solid is also soluble in strong acetic and nitric acids. Strong sulphuric acid dissolves it, with formation of a deep reddish-brown solution. With hydrochloric acid, cobaltous salt and chlorine are formed.

The cause of failure in the first attempt to oxidise an acid solution of cobaltous sulphate alone is not very evident. The only probable explanation seems to be that the solution had got warm. Certain it is that next morning there was no appearance of change of colour.

Having succeeded in getting the simple cobaltic sulphate, there was no difficulty in getting the alums. A saturated solution of cobaltous sulphate was electrolysed till a large quantity of cobaltic salt had separated. The temperature was then allowed to rise to about 20°, and dilute acid added to dissolve the solid which still remained. The roughly calculated quantity of ammonium sulphate in fine powder was now added (only a small proportion of the cobalt passes to the inner cell) and a weak current passed till this was practically all dissolved. The clear liquid was then decanted and cooled by a freezing mixture. In this way a large crop of minute, octahedral crystals of the alum was obtained, and separated and dried like the sulphate. By more slowly cooling, larger crystals, recognisable with the naked eye, or easily with a hand lens, separated; they had a fine deep blue colour. That they were regular octahedra was shown by their behaviour in polarised light. It was hardly necessary to analyse them, but the cobalt, total water (including that from the hydrogen of the ammonium), and sulphuric acid were estimated with the following results:—

	Found.	Calculated.
Co	12·05	12·09
SO_4................	40·1	39·62
H_2O (total)	52·6	52·00

In a similar way, the potassium compound was obtained. As would be expected, the alums behave towards water and acids like the cobaltic sulphate. They also decompose when they lose water. The crystals cannot be so completely freed from mother liquor by a porous plate, but may subsequently be pressed between filter paper, with which, however, they must not be left long in contact.

Cobaltic Ammonium Oxalate.

The experiments on the oxidation of cobaltous oxalate were also recommenced. As this salt is more soluble in ammonium than in potassium oxalate solution, the former was used. A small quantity was tried with a mixture of the two oxalates, with which a still stronger solution can be obtained. By fractional crystallisation of the oxidised solution, a solid compound was obtained which contained cobaltic, ammonium, and potassium oxalates, and agreed with the potassium compound described by Kehrmann. A much larger quantity of the pure ammonium compound was prepared. A hot saturated solution of cobaltous and ammonium oxalates was cooled and electrolysed, a considerable quantity of both the oxalates being added in a solid state. The inner cell was filled with oxalic acid solution, but, as a saturated solution of this acid is not very strong, the liquid in the inner cell soon becomes alkaline from free ammonia. To avoid this, a slow current of solution was kept flowing through the inner cell. With the oxalate it is quite unnecessary to cool the liquid. In this way a considerable quantity of dark-green solution was obtained. Alcohol was then added with the intention of fractionally precipitating the salts, and in this way the greater part of the ammonium oxalate and the cobaltous double salt were separated, but even a large quantity of alcohol did not precipitate the cobaltic compound. The solution was then left to concentrate spontaneously, during which operation a certain amount of decomposition took place. When a very strong solution had been obtained in this way, the evaporation was continued in a vacuum. Further quantities of impurities separated and ultimately a large mass of nearly black crystals was obtained and purified by recrystallisation. Analysis showed it to be the ammonium salt corresponding to the potassium salt obtained by

Kehrmann. The oxalic acid and the water were determined by combustion.

	Found.	Calculated for $Co_2(NH_4)_6(C_2O_4)_6,6H_2O$.
Co	13·80	13·61
NH_4..............	12·69	12·54
C_2O_4..............	61·20	61·31
H_2O (total)	38·76	37·62

The crystals are nearly black prisms which dissolve very readily in water, giving a dark-green solution. In thin films the salt exhibits dichroism—blue and green—as observed by Kehrmann in the case of the potassium salt. The solution was much more stable than was expected. It was only slowly decomposed on boiling, depositing cobaltous salt. Sulphurous acid, sulphuretted hydrogen, and even stannous chloride did not reduce it in the cold. Caustic alkalis gave a black precipitate on warming, but not immediately in the cold. With strong hydrochloric acid, the solution remained green, but changed to blue on warming, anhydrous cobaltous chloride being formed. The crystals effloresced when kept in a dry atmosphere (in a desiccator) at the ordinary temperature, yielding a bulky, green powder. A quantity which had been over sulphuric acid in a vacuum for several days was found to contain just about half as much water as the crystallised salt. The compound was found to be slowly decomposed by light, thus resembling the corresponding ferric salt. Some of the green powder which was left for several weeks in a tube was found to be bleached on the side towards the light, cobaltous salt and ammonium oxalate being formed, while the parts protected from the light remained bright-green.

Cobaltic Nitrate.

When a strong solution of cobaltous nitrate is electrolysed in a divided cell, it becomes of a deep indigo-blue, but soon returns to its original state when the current is stopped. Attempts to obtain a solid compound have not yet been successful, but the experiments are still being carried on.

In the last number of the *Berichte* (**24**, 2324), which has just been received, there is a paper, by Kehrmann and Pickersgill, "On the Cause of the Colour observed during the Electrolysis of Cobalt Oxalate Solution," in which they also prove that a cobaltic double oxalate is formed in this process. They have succeeded in isolating the potassium salt, and show that it is identical with that previously prepared by Kehrmann from cobaltic hydrate and potassium hydrogen oxalate. They did not use a divided cell, the operation being carried out practically as in the quantitative electrolytic deposition of cobalt.

University of Edinburgh,
August, 1891.

LXXIV.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

No. V. *The Persulphates.*

By HUGH MARSHALL, D.Sc., F.R S.E.

PERSULPHURIC anhydride, S_2O_7, was first described by Berthelot in 1878 (*Compt. rend.*, 86, 20, 277). He obtained it by subjecting a well-cooled mixture of sulphurous anhydride and oxygen to the "silent discharge" in an ozone tube. By treating the anhydride with water he obtained a solution which, while containing chiefly sulphuric acid formed by decomposition of the new substance, possessed oxidising properties, and might therefore be supposed to contain persulphuric acid. Subsequently (*ibid.*, 86, 71) he showed that a similar solution is formed at the anode during the electrolysis of fairly concentrated sulphuric acid. The oxidising properties of such a solution had been previously observed, but attributed to ozone and peroxide of hydrogen. By cautiously neutralising with barium hydrate and filtering, a solution was obtained which, on boiling, deposited barium sulphate, while free sulphuric acid, equivalent in quantity to the barium sulphate, remained dissolved. This seemed to prove that the substance was really an acid corresponding to the anhydride, although it was found impossible to obtain the salts in the solid state. Mendeléeff (*Bull. Soc. Chim.*, 38, 168), however, adopted a different view, holding that the new compounds were peroxides corresponding to barium peroxide, hydrogen peroxide, &c., and would not form salts.

Further papers on the subject have since been published by Moritz Traube (*Ber.*, **22**, 1518) and also by Richarz, chiefly with reference to the direct formation of peroxide of hydrogen. The former endeavoured to show that the formula adopted by Berthelot and also his view as to the nature of the compound were incorrect. He proposed the formula SO_4 and the name "sulphur holoxide." Early this year, however, I discovered a method of preparing solid persulphates, as mentioned in the preceding paper on cobaltic salts, and a short preliminary note on the potassium salt was read before the Royal Society of Edinburgh (*Proc. Roy. Soc. Edin.*, 18, 63). Recently, another paper, "On Sulphur Holoxide," has been published by M. Traube (*Ber.*, 24, 1764);* this has been promptly replied to by Berthelot (*Compt. rend.*, 112, 1481).

In the present paper I intend to describe, so far as they have been examined, those persulphates which I have as yet succeeded in preparing, as the completion of the investigation will probably require some considerable time. The salts described have not yet been subjected to proper crystallographic examination, so the exact crystalline forms are as yet doubtful. These and many other points must be reserved for a subsequent paper.

Potassium Persulphate.

The discovery of this salt, as already stated, was purely accidental. A fairly acid solution of cobalt and potassium sulphates was being electrolysed in a "divided" cell (this vol., p. 761), when, after a day or two, a quantity of small crystals separated. These, when filtered from the blue mother liquor, proved to be colourless, and were, therefore, supposed to be simply potassium sulphate. They were, however, washed with cold water, and a solution of a small quantity tested with barium chloride solution. This gave only a faint precipitate, but, on warming, barium sulphate slowly separated and chlorine was evolved. The solution also liberated iodine from potassium iodide and showed other oxidising actions. When heated, acid fumes were evolved and pure potassium sulphate remained. This seemed all to point to the salt being a persulphate, and analysis confirmed this view.

The next thing was to prepare, if possible, further quantities of the salt. A saturated solution of potassium hydrogen sulphate was electrolysed in the apparatus described and figured on p. 765, the inner cell being filled with dilute sulphuric acid. A current of 3—3½ ampères was employed, and in the course of two days a white, crystalline deposit began to form. This proved to be potassium persulphate. After a considerable quantity had collected, it was separated from the mother liquor by filtration through perforated platinum foil and then dried on porous plates. The mother liquor was then put back, the basin filled up with more of the original solution, and the process continued. A further deposit began to form in an hour or two, and after 24 hours the salt was again removed. This was repeated several times until a considerable quantity had been collected. Starting as above described, simply from the double sulphate, the product first obtained is finely granular, and is easily separated. As the mother liquor gets more and more acid, however, the deposit gets much finer and is apt to run through the perforated platinum along with the liquid.

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* In an abstract of Traube's paper which appeared in "Notes" of *Nature*, 44, 163, it is stated that Berthelot obtained *crystals* of persulphuric acid on the anode in the electrolysis of sulphuric acid. It is hardly necessary to say that this is erroneous; he obtained crystals of the *anhydride* by means of the "silent discharge."

The dry salt obtained in this way is somewhat impure, containing sulphate and free acid. A nearly pure product can be got with the earlier crops by washing them with cold water after filtering, but with the fine deposits this is hardly possible. In any case it is much better to recrystallise the salt. For this purpose it is treated with hot distilled water so as to obtain a nearly saturated solution, and this, after filtering as quickly as possible, is then rapidly cooled. During the treatment with hot water, slight decomposition takes place, but the amount is inconsiderable unless the solution itself be heated for some time. The solution deposits the salt in the form of minute prisms, which are collected and dried. By allowing the solution to cool slowly, large crystals, generally tabular, are deposited, though long prisms sometimes grow from the surface of the liquid. By spontaneous evaporation, large, flat tables can be obtained. The crystals appear to be asymmetric, and the minute prisms show, in polarised light, numerous examples of twinning. Large twinned crystals have also been observed, the twinning plane being the tabular face.

The composition of the salt is represented by the formula KSO_4. As already mentioned, potassium sulphate is left on ignition, oxygen and sulphuric anhydride being evolved. The percentage of the former was determined, the oxidising power estimated by standard ferrous sulphate and permanganate solutions, whilst the amount of oxygen evolved on heating was also measured. In the latter case the salt was placed in a test-tube provided with a double-bored cork. By one tube, pure carbonic anhydride was introduced, while by another the gases were passed into a nitrogen measuring tube filled with a strong solution of caustic alkali. When all the air was displaced, the salt was heated till non-absorbable gas ceased to be evolved. The volume of oxygen from a given weight of salt was thus obtained.

Results of analysis:—

	Found.	Calculated for KSO_4.
K_2SO_4	64·2	64·4
SO_4 (from extra oxygen found by titration).	35·5	35·6

1·422 gram gave, at 752 mm. and 15°, 63·1 c.c. of oxygen, weighing 0·0848 gram, equal to 5·96 per cent. Theory, 5·92 per cent.

As regards the correct molecular formula, it would appear to be KSO_4 and not $K_2S_2O_8$. Dr. James Walker has kindly made a series of conductivity determinations with dilute solutions and obtained results as follows:—

v.	μ.	Δ $(\mu_{1024} - \mu_{64})$
64	125·0	15·7
128	130·0	
256	135·6	
512	139 0	
1024	140·7	

In the case of potassium perchlorate, the corresponding value of Δ, as given by Ostwald, is 15·0, and in the two cases the values of μ are almost identical for the various concentrations.

Potassium persulphate is sparingly soluble in cold water. Three determinations of the solubility at zero were made in the manner recommended by Victor Meyer:—

I. 9·738 grams of solution gave on evaporation and ignition 0·1093 gram of potassium sulphate, equivalent to 0·1695 gram of persulphate.

II. 14·851 grams of solution gave 0·1664 gram of sulphate, equivalent to 0·2581 of persulphate.

III. 24·219 grams gave 0·269 gram of sulphate, or 0·4172 of persulphate.

Therefore, 100 parts of water at 0° dissolve (1) 1·77, (2) 1·77, (3) 1·75 parts of potassium persulphate.

In aqueous solution the persulphate gradually decomposes at the ordinary temperature, with formation of potassium hydrogen sulphate and liberation of oxygen, but the process is a very slow one. After three months, a solution, pure to start with, was found to contain a considerable proportion of sulphate. The greater part, however, was found to be still undecomposed. The pure solution is neutral to test papers, and the progress of the decomposition can be noticed by observing the amount of acid liberated. The solution gave, with chromic acid and permanganate solutions, no indications of the presence of hydrogen peroxide. Another saturated solution was left for several weeks in contact with pure metallic zinc, and there still remained a considerable quantity of persulphate. To the same liquid a little copper sulphate solution was added, so as to form a zinc-copper couple. Three days later, traces of persulphate still existed in the solution.

The solution does not yield a precipitate with any reagent such as would give rise to ordinary double decomposition resulting in the formation of an insoluble salt. In fact, potassium persulphate, like the perchlorate, seems to be less soluble than the corresponding salt of any other metal. Any precipitates which are formed are, therefore, due to complete decomposition of the persulphate. Thus a clear solution of persulphate, when mixed with one of a barium salt, slowly deposits barium sulphate, often forming a thin layer closely adhering to the sides of the tube, and very difficult to remove. This decomposition is very much accelerated by heating the liquid. Even then, however, it takes some time, and a solution which has been briskly boiled often gives, after filtering and again boiling, a considerable further precipitate.

A solution of a lead salt also deposits sulphate on warming it with the persulphate. If alkali be added to the mixture (not previously heated) and then warmed, the hydrate first thrown down is changed to peroxide. A solution of lead hydrate in potassium hydrate also yields a precipitate of lead peroxide if boiled with the persulphate.

With silver nitrate, no immediate precipitate is obtained, but the liquid gradually acquires an inky appearance, and, after some time, a black precipitate of peroxide of silver separates. The liquid at the same time becomes strongly acid. This action is apparently due to the fact that silver persulphate is decomposed by water like some other silver salts of acids of sulphur, sulphuric anhydride being removed:

$$AgSO_4 + H_2O = AgO + H_2SO_4.$$

The accumulation of acid seems to stop the action, as the cautious addition of dilute alkali produces a further precipitation. This reaction—noticed before the nature of the salt was known—was at first supposed to be a reducing one, with separation of metallic silver, and the behaviour with Fehling's solution was next observed. Here, on gently warming, a reddish precipitate separated. This was assumed to be cuprous oxide, but was in reality peroxide. Both of these peroxides decomposed with evolution of oxygen when they were allowed to stand in contact with the liquid. In the case of silver, the brown basic hydrate (or oxide) precipitated by alkalis is gradually turned black by solution of persulphate.

With neutral solutions of manganous and cobaltous salts, partial precipitation of higher oxides takes place on heating with persulphate. In the cold, the addition of alkali precipitates the lower oxides; but these immediately darken, forming manganese peroxide and cobaltic oxide respectively.

Solutions of nickel salts behave similarly in presence of alkali, but without the latter no precipitation takes place.

Ferrous sulphate solution is rapidly oxidised to ferric by persulphate solution. The green colour changes to brown, but this becomes much paler if acid be then added. It appears as if some basic salt were formed when the solution is neutral. With strong solutions, a considerable rise of temperature is noticeable, as is also the case when solid persulphate is added to strong ferrous sulphate solution.

Potassium iodide gives no immediate reaction with persulphate solution, but, after some seconds, the liquid becomes pale yellow, iodine being liberated. The reaction takes a considerable time before it is complete. It proceeds much more quickly, however, if the temperature is raised. The addition of dilute sulphuric acid seems to have little, if any, effect.

Organic colouring matters—litmus and turmeric, for example—are slowly bleached by a solution of persulphate. This is probably due to the action of free persulphuric acid liberated by partial decomposition.

Paper and cloth become quite rotten after being dipped in a solution of persulphate.

Potassium ferrocyanide becomes readily oxidised to ferricyanide when warmed with persulphate solution.

Alcohol, in presence of water, is oxidised to aldehyde when warmed with persulphate. A dilute solution of the latter is, however, somewhat slowly reduced by alcohol, even in presence of acid, and may be boiled with it without complete decomposition occurring immediately, as shown by its still liberating iodine from potassium iodide. Solid persulphate is not decomposed by absolute alcohol, in which it is insoluble, even on boiling. An attempt to convert benzyl alcohol into the aldehyde directly was also unsuccessful, the crystals of persulphate being practically unattacked at the boiling point of the former liquid.

Experiments performed for the purpose of determining the exact decomposition temperature gave no satisfactory result, owing to the apparent impossibility of getting absolutely pure, dry material. The method tried was as follows:—A fine glass tube, similar to those used for melting-point determinations, but much longer, was closed at one end. Into the bottom of this some finely-powdered persulphate was introduced. The tube was then exhausted, and mercury allowed to enter. The small quantity of air remaining separated the latter from the persulphate. The tube was then fastened to a thermometer, and the whole heated in a bath of sulphuric acid. The occurrence of decomposition would be shown by the rapid rise of the column of mercury, the motion due to the expansion of the small quantity of air being slight, and steady. The evolution of gas began, however, to be quite marked a little above 100°; but, even after heating to fully 250°, some persulphate remained undecomposed. It is easy to see that the least trace of moisture, or of acid, present in the salt would cause this behaviour, and the presence of these it seems to be impossible to avoid.

Potassium persulphate has a cooling, saline taste, but leaves a peculiar after-taste, possibly due to persulphuric acid.

Freshly-purified persulphate emits no odour, but, after being kept for some time, a peculiar smell is noticeable on opening the bottle. In the case of a not very pure product ozone is evolved slowly. Other persulphates, much more soluble in water, and not so easily freed from it, as, for instance, the ammonium salt, seem to decompose more readily; and here, also, sometimes ozone is evolved, whilst, in other cases, the above-mentioned peculiar odour is strongly marked. It would seem to be due to persulphuric acid or anhydride. On one occasion, when some lead persulphate decomposed suddenly, the vapours were very pungent, not resembling ozone in the least, and rapidly browned potassium iodide paper held near the salt. With the small quantity of substance and the rapid decomposition, it was impossible, however, to prove the presence or absence of a sulphur compound. Berthelot found that, even at 0°, persulphuric anhydride possessed considerable vapour pressure, and can be sublimed without decomposition.

When a solid persulphate is gently warmed with strong nitric or sulphuric acid, the oxygen liberated is evolved largely in the form of ozone. A similar evolution is also observed during the evaporation of strong solutions on the water-bath. With hydrochloric acid, chlorine is obtained in place of oxygen.

Ammonium Persulphate.

This salt is formed in a manner precisely similar to that of the potassium salt. The solution for electrolysis was prepared by saturating dilute sulphuric acid (about 1 to 6 by volume) with ammonium sulphate. As in the case of the potassium salt, it may be several days before persulphate begins to crystallise out, but after that, the separation goes on steadily. Here, also, the nature of the deposit varies with each succeeding crop. When, at length, the separation of the solid from the mother liquor becomes difficult, it is better, instead of simply adding more original solution, to use only about half of the mother liquor, and, after diluting it with water, to saturate with solid ammonium sulphate. The early deposits are much more granular than with the potassium salt, and it is exceedingly easy to collect them.

Owing to its great solubility, even at low temperatures, the purification of the salt is not so easy as that of the potassium compound. It is, in fact, rather difficult to obtain really pure specimens in quantity, and it does not keep so well as the potassium salt. If a saturated solution is evaporated in a vacuum at the ordinary temperature, long, thin prisms generally separate at first. These have a rhombic appearance, and, between crossed Nicols, show extinctions parallel to the axis. If left undisturbed, they grow more rapidly laterally than in the other directions, and assume the form of lozenge-shaped, apparently monosymmetric tables, having the plane of symmetry at right angles to the original prism axis. The crystals thus formed from solutions of the crude salt are generally large, and quite transparent. When this purer product is dissolved and recrystallised, the crystals obtained are generally large and badly formed, having a lamellar structure, which makes them non-transparent. Some of these have often the appearance of thick, rhombic prisms. Owing to their lamellar structure, they retain mother liquor, and, therefore, slowly decompose throughout their whole extent. To obtain a pure specimen, it is best to cool with ice a solution saturated at the ordinary temperature, or slightly higher. The greater part, however, remains in solution, and the mother liquor must be afterwards evaporated in a vacuum.

For the analysis of the salt, a weighed quantity was dissolved in water, evaporated to dryness, and redissolved. This solution was then titrated with standard baryta water to determine the amount of free acid. The remainder of the sulphate was then precipitated as barium salt, and the whole collected and weighed. The total SO_4 thus found should be double that found by titration. The ammonia was also determined.

	Found.	Calculated.
NH_4	15·6	15·8
SO_4 (total)	83·9	84·2
SO_4 (by titration)	42·3	43·1

As already stated, the salt is very soluble in cold water, and a very considerable fall of temperature takes place on dissolution. The following determinations of the solubility at 0° were made:—

I. 4·880 grams of solution gave, on evaporation, treating with ammonia solution, and drying, 2·085 grams of ammonium sulphate, corresponding to 1·799 grams of persulphate.

II. 2·887 grams gave, on heating as above, 1·229 grams of sulphate, corresponding to 1·06 of persulphate.

Therefore, 100 parts of water dissolve, at 0°, (1) 58·4, (2) 58 0, parts of ammonium persulphate.

The reactions of this salt resemble those of the potassium compound, but are often more marked, owing to the greater solubility.

Considerable quantities have been prepared, as it forms the starting point in the preparation of the other persulphates.

Barium Persulphate.

This salt is prepared by treating a saturated solution of ammonium persulphate with barium hydrate. For this purpose it is unnecessary to use recrystallised salt, the only impurities being sulphate and free acid, which cause no extra trouble. The pure crystallised hydrate is added in some excess, as the impurities require more than the same weight of persulphate does, and also because decomposition, which would liberate acid, takes place during the subsequent operations.

The mixture of solid and solution is well rubbed up in a mortar, and then a rapid stream of air is driven through. The hydrate displaces the ammonia, forming persulphate, which dissolves, and the sulphuric acid forms insoluble barium sulphate. When the greater part of the liberated ammonia has been driven off, the remainder is removed by placing the liquid over sulphuric acid in a vacuum. Here it may be left over night, and it will probably be found, next morning, that no more ammonia remains, provided enough barium hydrate has been employed. The excess of the latter is next removed by passing in a stream of carbonic anhydride, the bicarbonate formed being subsequently decomposed by again placing it in a vacuum for a short time. The solution, which now contains pure barium persulphate, is filtered off from the sulphate and carbonate and evaporated in a vacuum, but during this operation decomposition takes place, sulphate separating out and persulphuric acid becoming liberated; so that if the concentration takes a considerable time, it is advisable to occasionally neutralise with barium hydrate solution. As soon as crystallisation commences, the evaporation is discontinued, and the salt which has separated is redissolved in the minimum quantity of water. The neutral solution, after filtering, is then cooled by means of ice until no more crystals are obtained. The salt is thus obtained in beautiful, small prisms, which are collected and dried on porous plates or between filtering paper. The mother liquor is again concentrated in a vacuum. The salt prepared in this way is quite pure, and keeps better than when the crystals are obtained directly by evaporation of the solution. In the latter case, large, interlocking prisms are, as a rule, produced. These are transparent and hard, and generally deeply striated, so that it is difficult to make out their form, but those which are at all distinct have a monosymmetric appearance. The minute crystals obtained by cooling the solution also appear monoclinic when examined under the microscope, but between crossed Nicols show extinctions always parallel, or nearly so, to the prism axis. Sometimes, on evaporating in a vacuum, rosettes, in which the prisms radiate from a common centre, are obtained, as if crystallisation had taken place in a supersaturated solution.

The formula of the salt is $Ba(SO_4)_2,4H_2O$. In two different specimens the sulphate left on ignition was determined. In another, the percentage of barium was got from the amount of sulphate deposited on boiling the solution; the total SO_4 was then obtained by precipitating the filtrate with barium nitrate and adding the sulphate thus formed to the previous portion.

	Found.		
	I.	II.	Calculated.
$BaSO_4$ (on ignition)....	58·0	58·2	58·10

	Found.	Calculated.
Ba	33·7	34·16
SO_4 (total)..........	48·3	47·88
H_2O (by diff.)........	18 0	17·96

The last specimen has apparently been contaminated with some undecomposed ammonium salt.

In the course of a few days, the crystals gradually become milky from separation of sulphate; this change commences externally, and quickly spreads throughout the entire crystal, which crumbles to pieces, forming a moist, powdery mass. When once decomposition has fairly set in, it proceeds rapidly until all the barium exists as sulphate, but after this, the persulphuric acid which remains produces free sulphuric acid by its decomposition, and in presence of the latter the persulphuric acid is much more slowly decomposed, so that traces of it may still be present even after some weeks. Decomposition soon begins if the salt is kept in a dry atmosphere, so that attempts to prepare a less hydrated salt by placing it over sulphuric acid in a vacuum were fruitless. To preserve the crystals as long as possible, it was found best to keep them in an atmosphere which was always moist, wet filter paper being placed in the same vessel, but not in contact with the crystals. The salt itself is apparently not at all deliquescent.

Barium persulphate is very soluble in cold water. A single determination of the solubility at 0° was made, with the following result:—

> 5·598 grams of solution gave, on evaporation and ignition, 1·115 grams of barium sulphate, corresponding to 1·574 grams of anhydrous persulphate or 1·919 grams of crystallised salt. Therefore, 100 parts of water at 0° dissolve 39·1 parts of the former or 52·2 parts of the latter.

A control experiment was not performed, owing to the small quantity of material available at the time. The numbers will, however, give at least a fair approximation to the value. From the quantity of salt which crystallised out on cooling the solution, which was saturated at about 15°, it is evident that the solubility is very much higher at the latter temperature.

The salt evidently forms supersaturated solutions somewhat readily on evaporation in a vacuum. If a few drops of solution, placed on a slip of glass, be so treated, a gummy mass is obtained, which, when touched, slowly crystallises. Minute needles grow out radially from a common centre, forming fine rosettes, each of which shows a dark cross when viewed in polarised light. Pure solutions decompose gradually, somewhat slowly at first, when allowed to stand at the ordinary temperature. If a fairly dilute solution is heated, it generally remains clear till near the boiling point, when sulphate rapidly precipitates. It requires rather prolonged boiling, however, to destroy the last traces of persulphuric acid.

The behaviour of alcohol towards the salt is somewhat peculiar. If a few drops be added to an aqueous solution, it seems to accelerate the decomposition. It therefore seemed probable that the solid also would be decomposed when treated with alcohol. It was found, however, that the finely-powdered crystals dissolved in absolute alcohol, yielding a clear solution. This, when allowed to stand, slowly deposited a white solid; the action taking place rapidly when the solution was boiled. The solid was presumably barium sulphate, but, on adding water, it redissolved entirely, and this solution then slowly deposited sulphate. The persulphate was, therefore, not decomposed, but probably only dehydrated by the alcohol. This was found to be the case, as some of the dried deposit, when ignited, gave 65·39 per cent. of sulphate. The behaviour of a saturated aqueous solution, when treated with a large excess of alcohol, was then examined, when it was found that a similar product could be obtained. The liquid remained clear at first, but, on warming, a bulky precipitate separated. It was necessary to take several times as much absolute alcohol as solution, otherwise decomposition rapidly took place, free oxygen escaping, though aldehyde was also formed. In this case the product gave less sulphate on ignition—only 64·66 per cent.—and, on examining some under the microscope, crystals of the fully hydrated salt were noticed. These had, however, a "weathered" appearance, having apparently been externally dehydrated by the alcohol. The percentage of sulphate calculated for the formula $Ba(SO_4)_2,H_2O$ is 67·15, and for $Ba(SO_4)_2,2H_2O$ is 63 84, so that, in the case of each product, the quantity of sulphate found showed that 1 mol. H_2O, at most, was present in the compound. It was found that during the evaporation of the alcohol wetting it, the dehydrated salt again took up any water that might be present, and this fact might explain the percentage of water in the first case being higher than that required for a monohydrate. As it was possible, however, that the pure compound was really anhydrous, it was necessary to obtain a product which had no opportunity of re-forming the original salt. For this purpose some finely-powdered crystals were digested during several days with successive portions of cold absolute alcohol. The last portion of alcohol was then removed by pure ether dried over sodium; the greater part of the ether was then removed by decantation and the remainder by means of a current of dry air. A weighed portion of the residue gave, on ignition, 67·4 per cent. of sulphate. A monohydrate, as noted above, should yield only 67·15 per cent., but it was found that there was a small quantity of sulphate in the persulphate, as a portion, when dissolved in water, left a minute trace of insoluble matter. On endeavouring to further dehydrate a portion, by leaving it over sulphuric acid in a vacuum, decomposition rapidly ensued. There seems little doubt, therefore, that the compound obtained in this way has the formula $Ba(SO_4)_2,H_2O$. It is interesting to note that barium perchlorate crystallises with 4 mols. H_2O. Of these, three can be easily removed, but the last cannot be abstracted without complete decomposition of the salt. The crystalline perchlorate is likewise soluble in alcohol.

The alcohol with which the persulphate was digested was tested, and found to contain no barium, so that the monohydrated salt is quite insoluble in absolute alcohol. On the addition of potassium iodide to the alcoholic liquid, iodine was liberated, so that the persulphuric acid, formed by the decomposition of the small quantity of the persulphate which also yielded the barium sulphate found in the solid product, had apparently dissolved without being decomposed by the alcohol.

Solid barium persulphate is very readily decomposed by heat, gentle warming being sufficient. In the case of the monohydrated salt, a slight cloud is formed at the moment of decomposition, but only at a much higher temperature are acid vapours freely evolved. The quantity of water is just sufficient to form pure sulphuric acid,

$$2Ba(SO_4)_2,H_2O = 2BaSO_4 + 2H_2SO_4 + O_2,$$

and this, of course, even at the comparatively low temperature of decomposition, gives up a part of its sulphuric anhydride.

Lead Persulphate.

The comparative ease with which pure barium persulphate can be obtained is due to the insolubility of the sulphate, and as lead sulphate is also insoluble, the preparation of lead persulphate was next attempted. Owing, however, to the insolubility of the oxide and hydrate, as well as to other causes, this is a much more difficult matter. If oxide of lead is rubbed up in a mortar with a saturated solution of ammonium persulphate, considerable quantities of ammonia are liberated, but in a short time the mixture darkens from formation of peroxide of lead, and on treating with water and filtering, no soluble salt of lead is found in solution. It seemed, therefore, that the only practical method of obtaining the salt was to decompose a strong solution of barium persulphate with a slight excess of sulphuric acid in the cold, and then to neutralise the liquid with lead carbonate; this was tried and found to answer. The acid solution was not filtered off from the barium sulphate, the lead carbonate being simply added directly to the cold mixture. Brisk effervescence took place, but after this was over the liquid still had a marked acid reaction. This did not disappear if the mixture was left for a considerable time, and before very long darkening commenced from formation of the peroxide. The solution, which was found to contain a large quantity of the persulphate, was therefore filtered off and placed over sulphuric acid in a vacuum. The evaporation took a considerable time, and during the process lead sulphate separated out continuously; this was removed frequently by filtration. Owing to the decomposition, the liquid became more and more acid. Some barium hydrate solution was therefore added on one occasion, but not sufficient for complete neutralisation. It was expected that the barium would all be removed as sulphate by subsequent decomposition. Next morning the bottom of the dish was covered with a firm, coherent deposit, consisting of a mixture of barium sulphate and lead peroxide. Lead persulphate in strong solution would therefore appear to resemble the silver salt, requiring the presence of free acid to prevent deposition of peroxide. Ultimately a solid mass was obtained. This had a pearly lustre, but, though crystalline, no distinct form was observable. It was removed, quickly powdered, and then pressed between filter paper to remove as far as possible the small quantity of adhering liquid. The salt began to deliquesce, however, and was again placed in a desiccator over sulphuric acid. Here it was kept under diminished pressure for some hours, when it was found to have formed a firm, dry cake. It contained a small quantity of admixed sulphate, as shown by treating some with water, when a small residue remained. Free persulphuric acid was also present. A portion of the product was weighed out for the determination of the total lead sulphate and sulphuric acid obtained on decomposing the salt by evaporation of its solution. It was intended to estimate, subsequently, the ready-formed sulphate on a larger portion, and to make a direct determination of the water. Unfortunately, however, the remainder of the salt suddenly began to decompose with great rapidity, evolving pungent fumes which browned potassium iodide paper. The proportion of impurity could, therefore, not be determined. The analysis stated below can, consequently, give only an approximation to the composition of the salt, which at present remains doubtful.

		Calculated for	
	Found.	$Pb(SO_4)_2,2H_2O$.	$Pb(SO_4)_2,3H_2O$.
Pb	46·3	47 6	45·7
SO_4	43·5	44·1	42·4
H_2O (by diff.)	10·2	8·3	11·9

Allowing for the presence of other substances, the second formula appears the more probable. If correct, this would make the persulphate agree with the perchlorate, which crystallises with 3 mols. H_2O.

As already mentioned, the salt is very soluble in water, and deliquesces in a moist atmosphere. A solution gives, with alkalis, a white precipitate of hydrate which is rapidly oxidised to peroxide. Owing to the decomposition of the material, no other properties could be examined.

Other Persulphates.

The zinc salt was prepared in solution by double decomposition between zinc sulphate and barium persulphate in the proper proportions. On evaporating the filtered liquid over sulphuric acid in a vacuum, a mass of minute needles was obtained. This deliquesced on exposure to air, but contained a large proportion of sulphate mixed with the persulphate, and the two could not be separated with the comparatively small quantity of material to hand, on account of the great solubility of the sulphate and the continual decomposition.

A similar attempt to prepare the copper salt was made, but with no more satisfactory results. In this case, also, there was decomposition with formation of a considerable quantity of sulphate and free acid. Some barium carbonate was added in the hope that, by neutralising the acid (forming ultimately barium sulphate) it would decrease the rate of decomposition. The experiment was not successful, as double decomposition gradually took place, and, next morning, the barium was in solution as persulphate, and copper carbonate was deposited. A small quantity of solution of the copper salt was evaporated to dryness, and gave a blue, crystalline solid containing sulphate and persulphate; it deliquesced on removal from the desiccator.

Attempts to prepare sodium, lithium, and magnesium persulphates directly by electrolysis proved unsuccessful. In the case of the first two this seems to be due to the great solubility of the persulphates, as, in each case, the liquid was very highly oxidised; but the only salts which separated were normal and acid sulphates, which are, evidently, less soluble in the strongly acid liquid.

In the case of magnesium, a white, muddy deposit, which consisted of dehydrated sulphate, was obtained, but no trace of persulphate was observable. The mother liquor, also, did not seem to be very much oxidised; so that it is possible that magnesium persulphate cannot be prepared, even in solution, in this way.

The preparation in a pure state of such exceedingly soluble salts, where the sulphates also dissolve so readily in water, will, apparently, be a matter attended with some difficulty, and require working on a comparatively large scale. As the barium salt cannot be kept for more than a few days, it is necessary to prepare it as wanted.

Apart from the interest attaching to the salts themselves, the preparation of pure persulphates in a solid, crystalline form is of considerable theoretical interest and importance. It conclusively proves the correctness of Berthelot's views as to the composition and nature of the "persulphuric anhydride" and "persulphuric acid" prepared by him; that they are, in fact, entitled to the names which he gave them, and cannot be considered as peroxides, as held by Mendeléeff. The fact of the occurrence of a salt-forming oxide of sulphur having the formula S_2O_7 shows that we cannot adopt the rule as to the highest salt-forming oxide of an element which was previously supposed to exist as a deduction from the periodic law. Persulphuric acid can no more be classed as a peroxide than perchloric acid can. In fact, although the persulphates would seem not to be isomorphous with the perchlorates, they exhibit many close resemblances with them, in the matter of solubility, for instance.

Berthelot, in his last paper (*loc. cit.*), has already disposed of Moritz Traube's theory as to the formation of neutral "sulphur holoxide," SO_4, during the electrolysis of strong sulphuric acid solution. The only result given by the latter which points to the possibility of such a substance being present in the oxidised liquid, is that showing the ratio of oxidising power to sulphuric acid formed on decomposition, the sulphuric acid previously present having been removed by means of barium phosphate. As Berthelot points out, the amount of extra oxygen found might partially be due to the presence of peroxide of hydrogen. It is also possible that the solution was not completely decomposed on boiling, a result which seems not so highly improbable after the experiences with persulphate solutions already noted in this paper. All the other results stated by Traube agree perfectly on the assumption that persulphuric acid, HSO_4, is formed.

I hope, before long, to make a further communication to the Society on the subject of persulphates. Meanwhile, other salts—selenates, tellurates, nitrates, &c.—are being examined with a view to determining whether they, also, may not give more highly oxidised products when their solutions are electrolysed in a divided cell.

University of Edinburgh,
August, 1891.

LXXV.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

Acetylcarbinol.

By W. H. Perkin, Jun., Ph.D., F.R.S.

Although several members of the series of ketone alcohols have been isolated and described, it is surprising, in view of the great interest attaching to these compounds, that the first member of the series, acetylcarbinol (acetol, acetone alcohol), $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$, has hitherto been obtained only in aqueous solution.

In this form it has been obtained by the following reactions:—

1. When α-chlorallyl alcohol, $CH_2{:}CCl{\cdot}CH_2{\cdot}OH$, is dissolved in concentrated sulphuric acid, and the product distilled in a current of steam, a dilute aqueous solution of acetylcarbinol passes over (Henry, *Bl.*, **39**, 526).

2. When caustic potash is added to fused cane sugar or grape sugar in a retort, an aqueous distillate is obtained which contains acetylcarbinol (Emmerling and Lodges, *Ber.*, **16**, 837).

3. When monobromacetone, $CH_2Br{\cdot}CO{\cdot}CH_3$, is treated in aqueous solution with silver oxide, acetylcarbinol is formed. By the action of potassium carbonate on monobromacetone, Emmerling and Wagner (*Annalen*, **204**, 40) obtained a sweet substance, which was very soluble in water, reduced Fehling's solution, and which these authors supposed to be acetylcarbinol.

I have carefully repeated this latter experiment under very varied conditions, but, although I obtained a substance closely resembling the product described by Emmerling and Wagner, it was, certainly, not acetylcarbinol, as it did not distil without decomposition, and, on analysis, numbers were obtained which differed widely from those required by the formula $CH_3\cdot CO\cdot CH_2\cdot OH$.

Although acetylcarbinol itself has not been isolated, derivatives of this alcohol are well known; thus alkyl ethers of acetylcarbinol have been prepared from the corresponding propargyl compounds (Henry, *J.*, 1881, 506) by hydration by means of mercuric bromide, thus:—

$$CH{\vdots}C\cdot CH_2\cdot OC_2H_5 + H_2O = CH_3\cdot CO\cdot CH_2\cdot OC_2H_5;$$

and acetylcarbinyl acetate, $CH_3\cdot CO\cdot CH_2\cdot O\cdot C_2H_3O$, was long ago prepared by the same chemist (*Ber.*, **5**, 966), and by Zincke and Breuer (*Ber.*, **13**, 638), by digesting monochloracetone with potassium acetate in alcoholic solution:

$$CH_3\cdot CO\cdot CH_2Cl + CH_3\cdot COOK = CH_3\cdot CO\cdot CH_2\cdot O\cdot C_2H_3O + KCl.$$

Latterly, Laubmann (*Annalen*, **243**, 244—248) has shown that solutions of acetylcarbinol, when treated with phenylhydrazine, yield an oily hydrazine compound, which, when heated with excess of the reagent, is converted into acetolosazone,

$$CH_3\cdot C(N_2H\cdot C_6H_5)\cdot CH(N_2H\cdot C_6H_5).$$

The formation of this substance, which is identical with the phenylhydrazine compound of methylglyoxal, $CH_3\cdot CO\cdot COH$ (v. Pechmann, *Ber.*, **20**, 2543), proved conclusively the presence of acetylcarbinol in these solutions.

The difficulty experienced in obtaining acetylcarbinol by the hydrolysis of any of its compounds is due, in the first place, to the readiness with which it undergoes change when treated with reagents; and, secondly, to its extreme solubility in water, which renders extraction with ether or other solvents almost impossible, even in the case of moderately strong solutions.

In the course of a long series of experiments on the isolation of acetylcarbinol, extending over a number of years, it occurred to me that if chloracetone was boiled with water and some substance, such as barium carbonate, which, while capable of exercising a hydrolytic action, would, on account of its insolubility in water, be incapable of further action on the acetylcarbinol formed, very strong solutions of acetylcarbinol might be prepared from which the alcohol could be isolated by extraction with ether, thus:—

$$2CH_3\cdot CO\cdot CH_2Cl + BaCO_3 + H_2O = 2CH_3\cdot CO\cdot CH_2\cdot OH + BaCl_2 + CO_2.$$

This method was investigated by Dr. J. B. Tingle and myself, and small quantities of acetylcarbinol were actually obtained in this way;

but the yield was so small, and the isolation of the product so tedious, that at that time no further experiments were made on the subject.

On resuming the investigation, it was discovered that the hydrolysis of acetylcarbinyl acetate by means of water and barium carbonate took place much more readily than that of chloracetone, and, further, that dilute solutions of acetylcarbinol could be concentrated by distillation; taking advantage of these two facts, a method was devised by which large quantities of acetylcarbinol can be obtained in a comparatively short space of time.

This method, which is described in detail in this paper, is briefly as follows:—Acetylcarbinyl acetate is boiled in aqueous solution with barium carbonate until completely hydrolysed, the resulting product freed from barium acetate by distillation under reduced pressure, and the strong aqueous solution of acetylcarbinol thus obtained separated from the bulk of the water by careful fractionation. In this way nearly the whole of the water may be removed, and the resulting 90 per cent. acetylcarbinol, after drying over anhydrous sodium sulphate, and distillation under reduced pressure, can be readily obtained pure.

Acetylcarbinol is a peculiarly smelling, colourless oil which boils at 147°, and solidifies at low temperatures; it is miscible in all proportions with water; it reduces ammoniacal solution of nitrate of silver and Fehling's solution in the cold; sodium amalgam converts it quantitatively into methyl glycol:—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH + H_2 = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

I hope at a future date to communicate to the Society the results of further experiments on this interesting substance.

Acetylcarbinyl Acetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}C_2H_3O$.

This substance has already been prepared by Henry (*Ber.*, 5, 966), and by Zincke and Breuer (*Ber.*, 13, 638); it is readily produced by digesting monochloracetone with potassium acetate in alcoholic solution:

$$CH_3{\cdot}COOK + CH_3{\cdot}CO{\cdot}CH_2Cl = CH_3{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}C_2H_3O + KCl.$$

In preparing large quantities of acetylcarbinyl acetate, the method employed was that recommended by Zincke and Breuer, but slightly modified, in order to produce as large a yield as possible.

200 grams of pure, dry potassium acetate was mixed with about twice its weight of absolute alcohol, 185 grams of monochloracetone added, and the mixture heated on a water-bath in a flask connected with a reflux apparatus for two hours. After standing for 12 hours,

the product was separated from the precipitated potassium chloride by filtration on a filter-pump, the residue washed two or three times with small quantities of absolute alcohol, and the dark-coloured alcoholic liquors slowly distilled until the greater bulk of the alcohol had been removed; it was then rapidly distilled, under a pressure of 150 mm., from a strong, round-bottomed flask, heated by means of an oil-bath, until no more oily drops passed over. This method is far preferable to that recommended by Zincke and Breuer, namely, mixing the residue with water after distilling off the alcohol, and extracting with ether, as the acetate is not only miscible with water and difficult to extract by ether, but it is also, to a considerable extent, decomposed by solution in water, and great loss, therefore, occurs.

The crude acetylcarbinyl acetate, obtained by the above method, is readily purified by fractional distillation, first under reduced pressure, and then at the ordinary pressure.

Pure acetylcarbinyl acetate boils at 174—175° under a pressure of 760 mm., and at 137—138° under a pressure of 230 mm. Two specially purified preparations gave, on analysis, the following numbers:—

I. 0·1540 gram substance gave 0·0972 gram H_2O and 0 2913 gram CO_2.

II. 0·2402 gram substance gave 0·1473 gram H_2O and 0·4538 gram CO_2.

	Theory. $C_5H_8O_3$.	Found. I.	Found. II.
C	51·72 per cent.	51·57	51·50 per cent.
H	6·90 „	7·01	6·81 „
O	41·38 „	41·42	41·69 „

If the materials used in the above method of preparation are carefully dried, and precautions are taken to exclude moisture in the subsequent purification of the crude product, the yield obtained is about 80—85 per cent. of the theoretical; and this yield may be still further improved by using the alcohol from one operation for a subsequent preparation, as the small quantities of the acetate which always distil over with the alcohol may in this way be recovered.

Acetylcarbinyl acetate is a colourless, limpid liquid possessing a peculiar, sickly odour; it is miscible with water, and to some extent decomposed by it; the aqueous solution, on standing, acquires a very acid reaction. The density and magnetic rotation of this substance were determined by W. H. Perkin, sen., with the following results:—

Density:—d 4°/4° = 1·0912; d 10°/10° = 1·0849; d 15°/15° = 1·0803; d 20°/20° = 1·0760; d 25°/25° = 1·0719.

Magnetic Rotation.

	t.	Sp. rotation.	Mol. rotation.
	15·2°	0·9091	5·424
	13·2	0·9150	5·458
	13·0	0·9091	5·418
	13·0	0·9076	5·409
	13·0	0·9091	5·418
	13·5	0·9091	5·416
	13·0	0·9137	5·440
	13·0	0·9113	5·426
Average ..	13·4	0·9105	5·426

The theoretical magnetic rotation of acetylcarbinyl acetate may be calculated thus:—

Acetylcarbinyl acetate results from the substitution of one of the hydrogen atoms in acetone by the group $CH_3 \cdot COO$.

The value of this group replacing an atom of hydrogen may be deduced as follows:—

I. Magnetic rotation of octyl acetate	10·601
Magnetic rotation of octane (cal.)..............	8·692
Difference = Magnetic rotation of the group $CH_3 \cdot COO$, replacing hydrogen	1·909
II. Magnetic rotation of propyl acetate	5·487
Magnetic rotation of propane (cal.)	3·577
Difference = Magnetic rotation of the group $CH_3 \cdot COO$, replacing hydrogen	1·910

If now we add this value to the magnetic rotation of acetone = 3·514, we obtain 5·424 as the theoretical magnetic rotation of acetylcarbinyl acetate, a number which agrees very closely with that actually found, namely, 5·426.

Acetylcarbinol, $CH_3 \cdot CO \cdot CH_2 \cdot OH$.

In order to prepare acetylcarbinol from its acetate, numerous experiments were made with various hydrolysing agents under the most varied conditions, but it was soon discovered that most of these were worthless, on account of their decomposing action on the acetylcarbinol produced.

The best results were obtained with moist barium carbonate, and ultimately the following method, which I give in detail, was adopted as giving a very satisfactory yield of the ketone alcohol:—

160 grams of pure acetylcarbinyl acetate is dissolved in 300 c.c. of water, heated to boiling in a round-bottomed flask connected with a reflux apparatus, and pure, dry barium carbonate added, advantageously in the form of small pellets, in such a way that no further addition is made until the previous pellet has entirely dissolved. At the end of about three hours the reaction is complete, as is shown by the fact that the addition of a small quantity of barium carbonate to the boiling liquid causes no further evolution of carbonic anhydride. The product is filtered from any trace of undissolved barium carbonate, and distilled as rapidly as possible, under a pressure of 100 mm., from a round-bottomed flask, heated by means of a paraffin-bath, until no more liquid passes over, but care must be taken not to raise the temperature of the bath unnecessarily high, otherwise the residue in the flask, which still contains a considerable quantity of acetylcarbinol, and the treatment of which is described below, is apt to be decomposed.

The colourless distillate, which measures about 350 c.c., when tested with Fehling's solution, as described on p. 794, is found to contain about 15 per cent. of acetylcarbinol, or about 51 grams in all.

The residue in the distilling flask is dissolved in a little water and distilled in a rapid current of steam, the paraffin-bath being kept at about 120°.

The following table may serve as an example of the distillates collected, and the amount of acetylcarbinol contained in each as determined by titration:—

	Distillate collected.	Fehling's solution reduced by 2 c.c.	Percentage of acetylcarbinol.	Total amount of acetylcarbinol.
I ..	150 c.c.	38·5 c.c.	11·5	17·2 grams.
II ..	104 "	25·3 "	7·6	7·9 "
III ..	100 "	19·5 "	6·0	6·0 "
IV ..	280 "	11·0 "	3·3	9·2 "
V ..	210 "	5·5 "	1·7	3·5 "
			Total	.. 43·8 grams.

The total amount of acetylcarbinol obtained from 160 grams of acetylcarbinyl acetate was therefore approximately 94 grams, whereas theoretically it should have been 103 grams; the hydrolysis by means of moist barium carbonate may therefore be considered as nearly quantitative.

In preparing large quantities of acetylcarbinol, the treatment of the aqueous solutions obtained as described above was approximately as follows:—

All the solutions containing from 6—7 per cent. of acetylcarbinol were first very slowly distilled from a large, round-bottomed flask fitted with a very long colonna, until the residue on titration was found to contain from 9 to 10 per cent. of the ketone alcohol. This residue was then mixed with other solutions of the same strength and the concentration continued until ultimately a residue was obtained which contains over 90 per cent. of acetylcarbinol.

In one series of experiments, in which 1 kilo. of pure acetylcarbinyl acetate was employed, the concentration of the aqueous solutions took about 14 days, and upwards of 450 grams of 90—95 per cent. acetylcarbinol was obtained, together with large quantities of weak solutions. These weak solutions, when they contain less than 5 per cent. of acetylcarbinol, are best employed, instead of water, in decomposing fresh quantities of acetylcarbinyl acetate, as their concentration is not profitable.

In order to prepare pure acetylcarbinol, the 90—95 per cent. product is dissolved in pure ether, the ethereal solution allowed to stand over anhydrous sodium sulphate for 24 hours, filtered, the ether slowly distilled off, and the residue fractioned under reduced pressure. Almost the whole passes over between 90° and 105°, under a pressure of 150 mm., at the first distillation, leaving, however, always a small residue in the retort, and on repeated fractionation pure acetylcarbinol is readily obtained boiling constantly at 96—97° (150 mm.).

The following results were obtained on analysis:—

I. 0·1383 gram substance gave 0·1026 gram H_2O and 0·2460 gram CO_2

II. 0·2081 gram substance gave 0·1539 gram H_2O and 0·3690 gram CO_2.

III. 0·1614 gram substance gave 0·1180 gram H_2O and 0·2890 gram CO_2.

IV. 0·1890 gram substance gave 0·1390 gram H_2O and 0·3400 gram CO_2.

V. 0·1700 gram substance gave 0·1244 gram H_2O and 0·3050 gram CO_2.

	Theory.	Found.				
	$C_3H_6O_2$	I.	II.	III.	IV.	V.
C	48·65 p. c.	48·51	48·36	48·83	49·05	48·93 p. c.
H	8·10 „	8·24	8·21	8·12	8·17	8·13 „
O	43·24 „	43·25	43·43	43·05	42·78	42·94 „

The vapour density of this substance, determined by Hofmann's method in toluene vapour, gave the following results:—

	Theory. $C_3H_6O_2$	Found. I.	Found. II.
D......	37·0	34·0	34·5

The molecular weight of acetylcarbinol was also determined by Raoult's method, using acetic acid as the solvent; the results obtained were the following:—

Substance taken	0·7660 gram.
Acetic acid	54·427 ,,
Depression of melting point ..	0·654°.

Molecular weight of substance found from the above data..	85
Theory for $C_3H_6O_2$..............	74

Acetylcarbinol is a colourless oil of a faint, sickly odour closely resembling that of the acetate; it boils constantly at 105—106° under a pressure of 200 mm. with very slight decomposition, and at about 147° under the ordinary pressure, but in the latter case not without decomposition, as a residue of high boiling point is always left in the retort. This residue, which probably contains condensation products of acetylcarbinol, on long standing, deposits crystals which have not yet been examined.

In a freezing mixture of powdered ice and hydrochloric acid, acetylcarbinol becomes quite thick, like glycerol, and on one occasion the substance solidified to a hard, crystalline mass.

It mixes with water, alcohol, and ether in all proportions, but is not precipitated from its aqueous solution by potassium carbonate, as is the case with solutions of acetopropyl alcohol and acetobutyl alcohol. The aqueous solution reduces ammoniacal silver solution and Fehling's solution in the cold; in the latter case the copper solution often remains unaltered for some seconds after mixing with the acetylcarbinol solution, particularly when this is weak, and then all at once reduction sets in. In some quantitative experiments it was found that 0·1 gram of acetylcarbinol dissolved in 50 c.c. of distilled water reduced about 16·5—16·6 c.c. of Fehling's solution (1 c.c. contains 0·03464 gram $CuSO_4,5Aq = 0·005$ gram grape sugar), but it is extremely difficult to accurately detect the end point of the reaction, as the solution becomes slightly yellowish during the reduction. According to Zincke (*Ber.*, 13, 2344), lactic acid is formed during this decomposition, thus :—

$$CH_3·CO·CH_2·OH + O = CH_3·CH(OH)·COOH;$$

and the amount of Fehling's solution reduced in the above experiments gives approximately 1 atom of oxygen to 1 mol. of acetylcarbinol.

Fehling's solution may, therefore, be used as a valuable test of the strength of aqueous acetylcarbinol solutions, and for this purpose about 2 c.c. of a weak solution (to 10 per cent.), or 1 c.c. of a stronger solution, is diluted with 50 c.c. of water, heated to about 80°, and Fehling's solution run in, as in the estimation of sugar, using, however, a flask instead of a porcelain dish, to avoid evaporation; the strength of the solution may then be roughly calculated from the data given above.

The determination of the density and magnetic rotation of acetylcarbinol was undertaken by W. H. Perkin, senr., and the following are the results of his experiments.

Density:—$d\,4^\circ/4^\circ = 1·0904$; $d\,15^\circ/15^\circ = 1·07915$; $d\,25^\circ/25^\circ = 1·07069$.

Magnetic Rotation.

	t.	Sp. rotation.	Mol. rotation.
	15·5°	0·9571	3·647
	"	0·9595	3·656
	"	0·9550	3·640
	"	0·9624	3·668
	"	0·9543	3·637
	"	0·9580	3·651
Average ..	15·5	0·9577	3·650

The magnetic rotation of acetylcarbinol may be calculated from that of methyl alcohol by adding the value of the acetyl group replacing hydrogen This latter value may readily be obtained thus:—

Magnetic rotation of ethyl acetoacetate	6·501
" " ethyl acetate................	4·462
Difference = Value of the acetyl group replacing hydrogen	2·039

The magnetic rotation of methyl alcohol is 1·640, and this added to 2·039 gives 3·679 as the magnetic rotation of acetylcarbinol, a number which agrees well with that actually found, namely, 3·650.

Preparation of Acetylcarbinol from Monochloracetone.

The first sample of acetylcarbinol obtained was prepared by Dr. J. B. Tingle and myself (Proc., 73, 156) from monochloracetone by hydrolysis with water and precipitated barium carbonate; the following is an outline of the process adopted:—

25 grams of monochloracetone is slowly added from a dropping funnel to 200 c.c. of water containing an excess of freshly-precipitated barium carbonate in suspension, the whole being vigorously boiled during the operation. As soon as the monochloracetone has dissolved, and the evolution of carbonic anhydride has practically ceased, the liquid is filtered, and the resulting, almost colourless solution distilled.

The distillate is again treated with chloracetone and barium carbonate, and again distilled, the operation being repeated until 150 grams of chloracetone has been decomposed. The resulting moderately concentrated solution of acetylcarbinol is saturated with potassium carbonate, and extracted at least 50 times with pure ether. The ethereal solution is thoroughly dried over ignited potassium carbonate, and is then slowly evaporated; a colourless oil remains, the greater part of which, on distillation, passes over between 140° and 150°. On refractioning, a considerable quantity was obtained, boiling at 145—150°, which gave, on analysis, numbers agreeing with the formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$:—

0·1546 gram substance gave 0·1160 gram H_2O and 0·2766 gram CO_2.

	Theory. $C_3H_6O_2$.	Found.
C.......	48·65 per cent.	48·73 per cent.
H.......	8·10 „	8·33 „
O.......	43·24 „	42·94 „

The vapour density of this product was determined by Hofmann's method in xylene vapour, with the following results:—

	Theory.	Found.	
	$C_3H_6O_2$.	I.	II.
D..........	37	35	34

The amount of acetylcarbinol obtained by this method was very small, but the yield could no doubt be much improved by concentrating the aqueous solution and isolating the ketone alcohol in the manner described on p. 792.

Action of Phenylhydrazine on Acetylcarbinol.

Acetylcarbinol Osazone, $CH_3{\cdot}C(N_2H{\cdot}C_6H_5){\cdot}CH(N_2H{\cdot}C_6H_5)$.

The phenylhydrazine compound of methylglyoxal (acetylcarbinol osazone) was first prepared by v. Pechmann (*Ber.*, **20**, 2543), by warming together aqueous solutions of methylglyoxal (or nitrosoacetone) and phenylhydrazine, thus:—

$$CH_3{\cdot}CO{\cdot}COH + 2N_2H_3{\cdot}C_6H_5 = CH_3{\cdot}C(N_2H{\cdot}C_6H_5){\cdot}CH(N_2H{\cdot}C_6H_5) + 2H_2O.$$

Subsequently, H. Laubmann (*Annalen*, **243**, 244—248) obtained the same substance by treating a solution of acetylcarbinol with phenylhydrazine. In order to prove that the substance described as acetylcarbinol in this paper really has this constitution, 5 grams of the pure substance was dissolved in 50 grams of water, a strong solution of phenylhydrazine added in excess, and the oily phenylhydrazine compound which separated digested in a sealed tube with excess of phenylhydrazine at 100—105°.

The crude osazone thus obtained, after recrystallisation from dilute alcohol, gave the following numbers on analysis:—

0·1790 gram substance gave 33·8 c.c. nitrogen; $t = 16°$; bar. = 761 mm.

	Theory. $C_{15}H_{16}N_4$.	Found.
N	22·22 per cent.	22·20 per cent.

This substance melted at 145°, and was identical in its properties with the compound described by v. Pechmann and H. Laubmann (*loc. cit.*).

Reduction of Acetylcarbinol.

Formation of Methylglycol, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$.

Acetylcarbinol is readily reduced by sodium amalgam with formation of methylglycol, thus:—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH + H_2 = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

In carrying out this experiment, a quantity of a 10 per cent. solution of acetylcarbinol was transferred to a flat porcelain dish, and treated with twice the calculated quantity of 2½ per cent. sodium amalgam, in small portions at a time. As soon as the reduction was complete, the product was separated from the mercury, neutralised with hydrochloric acid, and slowly distilled from a flask, furnished with a long colonna, and heated by a paraffin-bath, until the residue deposited a quantity of crystals of salt. This residue was next mixed with absolute alcohol, an equal bulk of ether added, and after standing for 24 hours the solution of the glycol was separated from the precipitated salt by filtration, and evaporated; the crude oily product was then purified, first by distillation in a vacuum, and then at the ordinary pressure. In this way an almost theoretical yield of methylglycol was obtained, which boiled constantly at 188°.

The analysis gave the following results:—

0·1798 gram substance gave 0·1696 gram H_2O and 0·3132 gram CO_2.

	Theory. $C_3H_8O_2$.	Found.
C.......	47·37 per cent.	47·50 per cent.
H.......	10·53 ,,	10·49 ,,
O.......	42·10 ,,	42·01 ,,

Methylglycol was first obtained by Würtz (*Ann. Chim. Phys.* [3], **55**, 438) from propylene bromide, by digesting it with silver acetate, and subsequent hydrolysis of the acetate formed; Hartmann (*J. pr. Chem.* [2], **16**, 383) obtained the same substance in small quantity by boiling propylene bromide with an aqueous solution of sodium carbonate.

The boiling point and other properties of the substance obtained from acetylcarbinol are identical with those ascribed by Würtz to methylglycol.

The density and magnetic rotations of methylglycol were determined by W. H. Perkin, sen.

Density:—$d\,4°/4° = 1·0464$; $d\,15°/15° = 1·0389$; $d\,25°/25° = 1·03367$.

Magnetic Rotation.

	t.	Sp. rotation.	Mol. rotation.
	15·5°	1·0058	4·098
	,,	1·0061	4·099
	,,	1·0055	4·096
	,,	1·0018	4·082
	,,	1·0042	4·091
Average ..	15·5	1·0047	4·093

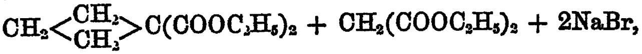
LXXVI.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

Action of Methylene Iodide on the Disodium Compound of Ethyl Pentanetetracarboxylate. Synthesis of Hexamethylene Derivatives.

By W. H. PERKIN, Jun., Ph.D., F.R.S.

WHEN trimethylene bromide is treated with the mono-sodium compound of ethyl malonate, the reaction proceeds in two distinct phases (Trans., 1887, 51, 1, 241). In the first place, ethyl tetramethylenedicarboxylate is formed with regeneration of a corresponding amount of ethyl malonate, thus:—

$$2CHNa(COOC_2H_5)_2 + CH_2Br\cdot CH_2\cdot CH_2Br =$$



$$CH_2<\substack{CH_2\\CH_2}>C(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 + 2NaBr,$$

whilst the second reaction consists in the production of ethyl pentanetetracarboxylate, thus:—

$$2CHNa(COOC_2H_5)_2 + CH_2Br\cdot CH_2\cdot CH_2Br =$$
$$(COOC_2H_5)_2CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(COOC_2H_5)_2 + 2NaBr.$$

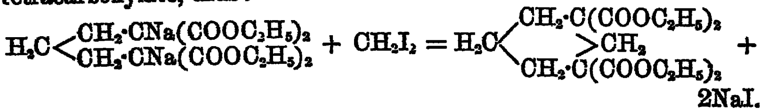
This ethereal salt has been found to be of very great service in synthetical experiments, owing to the fact that when treated with sodium ethylate, it yields a disodium compound,

$$(COOC_2H_5)_2CNa\cdot CH_2\cdot CH_2\cdot CH_2\cdot CNa(COOC_2H_5)_2,$$

which reacts readily with alkyl haloids yielding, indirectly, derivatives of pimelic acid (see the next paper), and which has also been employed in the synthesis of pentamethylene derivatives (Trans., 1887, 51, 241).

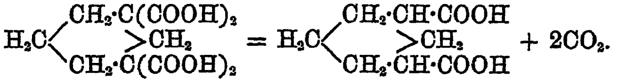
In the course of these experiments it seemed probable that very interesting results might be obtained by the study of the action of methylene iodide, ethylene bromide, trimethylene bromide, and other similar alkylene haloids on this disodium compound, and I beg now to lay before the Society a short account of the results which have been obtained in the case of methylene iodide, reserving for a future paper the consideration of the action of the other alkylene haloids on this disodium compound.

At 100°, methylene iodide reacts readily with an alcoholic solution of the disodium compound of ethyl pentanetetracarboxylate with separation of sodium iodide and formation of ethyl hexamethylenetetracarboxylate, thus:—



$$H_2C<\substack{CH_2\cdot CNa(COOC_2H_5)_2\\CH_2\cdot CNa(COOC_2H_5)_2} + CH_2I_2 = H_2C\left<\begin{array}{l}CH_2\cdot C(COOC_2H_5)_2\\ \qquad >CH_2\\ CH_2\cdot C(COOC_2H_5)_2\end{array}\right. + 2NaI.$$

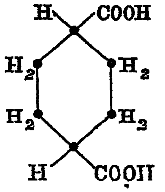
This ethereal salt, on hydrolysis, yields the corresponding hexamethylenetetracarboxylic acid, and this beautifully crystalline substance, when heated at 200—220°, is decomposed with evolution of 2 mols. of CO_2 and formation of *two isomeric* hexamethylenemetadicarboxylic or *hexahydroisophthalic acids :*



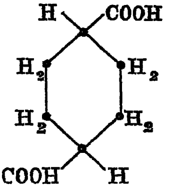
$$H_2C<\begin{matrix}CH_2\cdot C(COOH)_2\\ >CH_2\\ CH_2\cdot C(COOH)_2\end{matrix} = H_2C<\begin{matrix}CH_2\cdot CH\cdot COOH\\ >CH_2\\ CH_2\cdot CH\cdot COOH\end{matrix} + 2CO_2.$$

In order to understand this interesting decomposition, it will be well to compare these compounds with the corresponding hexahydroterephthalic acids, which have been so carefully investigated by Baeyer.

Baeyer, in his classical researches on the reduction of terephthalic acid (*Annalen*, **245**, 103 ; **251**, 257), has shown that hexahydroterephthalic acid, which contains two *relatively* asymmetrical carbon atoms (*Annalen*, **245**, 130), is capable of existing in two modifications; these he formulates and designates thus :—*



Maleinoid (or Γ^{cis})
hexahydroterephthalic acid.



Fumaroid (or $\Gamma^{cistrans}$)
hexahydroterephthalic acid.

The Γ^{cis} or maleïnoid form is the labile modification, as it is converted into the $\Gamma^{cistrans}$ or fumaroïd form by heating with concentrated hydrochloric acid at 180°. The former is readily soluble in water, melts at 160°, and crystallises in large crystals like maleïc acid; the latter is sparingly soluble in water, sublimes on heating, and crystallises in short prisms, like fumaric acid.

Similarly, hexahydrophthalic acid, trimethylenedicarboxylic acid [1 : 2], the symmetrical substitution derivatives of succinic acid, and other analogously constituted acids have been found to exist in structurally isomeric forms, and in each case the evidence has been in favour of the assumption that the higher melting and less soluble isomeride is the $\Gamma^{cistrans}$ or fumaroïd modification.

An examination of the formula of hexamethylenemetadicarboxylic acid shows at once that this acid also contains two *relatively* asymmetrical carbon atoms, and this fact would lead to the supposition that this acid must also occur in two modifications, thus:—

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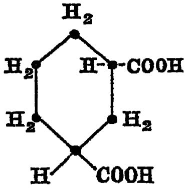
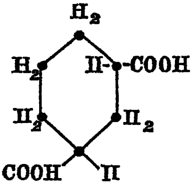
* The dots represent carbon atoms as in Baeyer's paper.



Maleïnoïd (or Γ^{cis}) hexamethylenemetadicarboxylic acid.

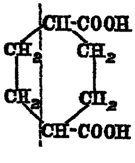


Fumaroïd (or $\Gamma^{cistrans}$) hexamethylenemetadicarboxylic acid.

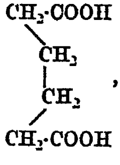
The investigation of the substance obtained from hexamethylenetetracarboxylic acid by the elimination of 2 mols. of CO_2 has shown that this product is, as theory indicates, a mixture of two isomeric acids, which may be separated by repeated recrystallisation, or better, by means of their calcium salts.

Of these two acids, the more soluble isomeride, which melts at 118—120°, was at first thought to be the Γ^{cis} or maleïnoïd acid, in which case the less soluble acid, which melts at 161—163°, would be the corresponding $\Gamma^{cistrans}$ or fumaroïd modification. On carefully examining the properties of these two acids, results were obtained which, as it appears to me, prove that the reverse is the case, and that the acid which has the higher melting point and lesser solubility must be represented as the maleïnoïd form.

Baeyer, in the course of his experiments on the constitution of benzene, was led to the conclusion that the reduction products of terephthalic acid no longer behave as benzene derivatives; they show, on the contrary, the properties of saturated and unsaturated compounds of the fatty series, even in the minutest details (*Annalen*, **251**, 257); thus hexahydroterephthalic acid may be compared with adipic acid:



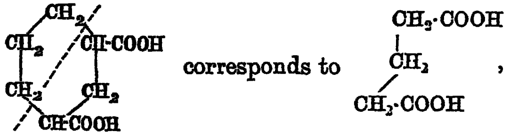
corresponds to



,

and as adipic acid gives no anhydride, so also no anhydride could be obtained from Γ^{cis} hexahydroterephthalic acid (*Annalen*, **245**, 174).

Hexamethylenemetadicarboxylic acid may, on the other hand, be compared with glutaric acid:



but glutaric acid, as Markownikow has shown (*Jour. Russ. Chem. Soc.*, 9, 283), readily yields an anhydride when heated with acetyl chloride; it therefore follows, if the analogy between the two acids holds good, that hexamethylenemetadicarboxylic acid should also give an anhydride.

On subjecting this hypothesis to the test of experiment, it was found that not only does the acid of lower melting point give an anhydride, but that both the isomeric hexamethylenemetadicarboxylic acids, when treated with acetyl chloride, yield with great ease *the same* anhydride, and this anhydride, when dissolved in water, is converted quantitatively into the acid melting at 161—163°, which must therefore be the Γ^{cis} or maleïnoïd acid. By conversion into the anhydride, and subsequent decomposition of this substance by water, it is thus possible to convert the $\Gamma^{cistrans}$ acid (m. p. 118—120°) quantitatively into the isomeric Γ^{cis} acid (m. p. 161—163°).

In discussing the nature of the hexahydroterephthalic and hexahydrophthalic acids, both of which exist in isomeric forms, Baeyer lays great stress not only on the anhydride formation, but also on the behaviour of the acids when heated with hydrochloric acid at 180°, as a means of distinguishing the Γ^{cis} and $\Gamma^{cistrans}$ modifications. In both cases under these circumstances, the lower melting or more soluble isomeride is converted into the higher melting and less soluble modification; the former Baeyer represents as the Γ^{cis} or maleïnoïd acid, the latter as the $\Gamma^{cistrans}$ or fumaroïd acid.

With a view to obtaining further evidence as to the nature of the two isomeric hexamethylenemetadicarboxylic acids, it was therefore important that the action of hydrochloric acid on the two acids should be carefully investigated. The results obtained in this investigation were very remarkable; the $\Gamma^{cistrans}$ acid of low melting point is converted by this treatment in part into the Γ^{cis} acid of high melting point, and the acid of high melting point is similarly, in part, converted into the acid of low melting point, but in both cases a considerable quantity of the original acid remains unchanged, and it would seem probable that the conversion of each modification into the other goes on until a certain equilibrium has been established, and then hydrochloric acid has no further action.

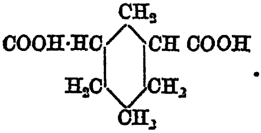
The only direct evidence at present obtained which throws any light on the constitution of these two hexamethylenedicarboxylic acids is, therefore, the fact that the anhydride, which is apparently equally readily obtained from each, and which must be the anhydride of the maleïnoïd acid, when dissolved in water, yields the acid melting at 161—163°, just as maleic anhydride, when dissolved in water, yields maleïc acid.

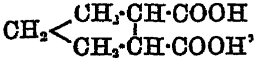
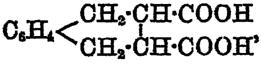
Therefore, as no evidence to the contrary has as yet been obtained, the acid melting at 161—163° is assumed to be r^{cis} hexamethylenemetadicarboxylic acid, and the acid melting at 118—120° is represented as $r^{cistrans}$ hexamethylenemetadicarboxylic acid.

So far it has been assumed that these acids are derivatives of hexamethylene, and there can be no doubt that this is the case, from the following considerations:—

1. Potassium permanganate is without action on dilute sodium carbonate solutions of these acids at the ordinary temperature, and, therefore, these acids cannot be unsaturated compounds (Baeyer, *Annalen*, **245**, 146).

2. These acids are capable of yielding anhydrides. This is only possible when the carboxyl groups in the original pimelic acid are approximated: and this can only be brought about by the formation of a ring in such a way that the carboxyl groups, which were originally separated by five carbon atoms, are now, by insertion of a methylene group and formation of a ring, only separated by three carbon atoms, as in glutaric acid:

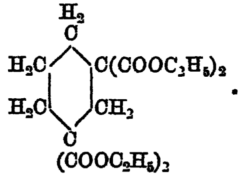
$COOH\cdot CH_2\cdot CH_2\,CH_2\cdot CH_2\cdot CH_2\cdot COOH$ becomes 

Further experiments on these interesting acids are in progress, and it is proposed to include also a study of pentamethylenedicarboxylic acid,  $CH_2<\begin{matrix}CH_2\cdot CH\cdot COOH\\ CH_2\cdot CH\cdot COOH\end{matrix}$, and tetrahydronaphthalenedicarboxylic acid,  $C_6H_4<\begin{matrix}CH_2\cdot CH\cdot COOH\\ CH_2\cdot CH\cdot COOH\end{matrix}$, with a view to determining whether these two substances are also capable of existing in structurally isomeric modifications.

It is unfortunate that, owing to the formation of bye-products of complicated constitution, the yield of the hexamethylenedicarboxylic acids obtained by the method described in this paper is so small, but it is hoped that, by varying the conditions employed, this yield may be ultimately improved.

In conclusion, I must express my thanks to Mr. Bertram Prentice for his very valuable help in carrying out this investigation.

Ethyl Hexamethylenetetracarboxylate [1 : 1 : 3 : 3],



In preparing this ethereal salt, the following quantities were used in each operation :—

Ethyl pentanetetracarboxylate..........	36·0 grams.
Sodium (dissolved in 50 grams of alcohol)	4·6 „
Methylene iodide	28·0 „

The ethyl pentanetetracarboxylate was mixed with the cold solution of the sodium ethylate in a soda-water bottle, the methylene iodide then added, the bottle securely corked and tied down, and warmed in a water-bath to about 50° with frequent agitation, until the layer of methylene iodide, which separates out on the bottom of the bottle, has completely dissolved. The water was then slowly raised to the boiling point, and the bottle kept at this temperature for six hours.

The product was then mixed with water, extracted three times with ether, the ethereal solution washed with water containing a little sulphurous acid (to remove traces of iodine), dried over calcium chloride, evaporated, and the resulting oil, which weighs about 34 grams, purified by fractionation under reduced pressure (50 mm.). A considerable quantity of a thick oil was thus obtained, which boiled at 235—255° (50 mm.), but there was a large, dark-coloured residue in the retort, which could not be distilled without decomposition. On refractioning the distillate, the product was ultimately obtained pure, as a colourless oil, boiling constantly at 243—245° under a pressure of 50 mm. This preparation gave the following numbers on analysis :—

I. 0 1662 gram substance gave 0·1188 gram H_2O and 0·3538 gram CO_2.

II. 0 1723 gram substance gave 0·1195 gram H_2O and 0·3680 gram CO_2.

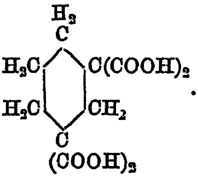
	Theory. $C_{18}H_{28}O_8$	Found. I.	II.
C	58 06 per cent.	58·33	58·25 per cent.
H........	7·53 „	7 94	7 70 „
O	34·40 „	33·73	34 05 „

The molecular weight of this ethereal salt was determined by Raoult's method with the following result, using acetic acid as the solvent:—

Weight of substance taken	1·1417 grams.
Weight of acetic acid....................	45·37 "
Melting point of the acetic acid	15·959°
Melting point of the mixture	15·685°
Depression of the melting point	0·274°
Molecular weight calculated from these data	= 359
Theory for $C_{18}H_{28}O_8$.....................	= 372

Ethyl hexamethylenetetracarboxylate is a thick, colourless oil, resembling ethyl pentanetetracarboxylate in its general properties. It is readily hydrolysed by boiling with alcoholic potash, with formation of the potassium salt of hexamethylenetetracarboxylic acid [1 : 1 : 3 : 3].

Hexamethylenetetracarboxylic Acid [1 : 1 : 3 : 3],



The purification of the crude product of the action of methylene iodide on the sodium compound of ethyl pentanetetracarboxylate, by fractionation, is always attended with great loss, as the oils of high boiling point contained in this crude product retard the distillation of the ethyl hexamethylenetetracarboxylate, and if the temperature is raised sufficiently high to distil over all the ethereal salt, rapid decomposition sets in. It is possible, however, to avoid this distillation, as considerable quantities of hexamethylenetetracarboxylic acid may be prepared directly from the crude ethereal salt in the following way:—

The crude ethereal salt (1 mol.) is gradually added to a methyl alcoholic solution of pure potassium hydrate (6 mols.), contained in a flask, and the mixture, as soon as the somewhat violent reaction has subsided, heated to boiling in a reflux apparatus on a water-bath for four hours. The alcohol is then distilled off, the residue dissolved in water, and evaporated on a water-bath till quite free from alcohol, the cold aqueous solution acidified with hydrochloric acid, all rise of temperature being avoided by cooling with water, and the product extracted at least 20 times with ether.

A curious phenomenon is noticeable during this operation; the liquid separates into three layers; the upper layer is the ethereal extract, the lower one the aqueous solution of the salts, and the middle layer is a thick, brownish-coloured oil, which, on shaking with ether, dissolves only to a small extent. This syrupy substance has only been superficially examined; it consists apparently of an acid of very complicated constitution, which evidently can be purified only with great difficulty.

The ethereal extract is dried over calcium chloride, evaporated to a small bulk, and allowed to stand in a cool place for a week, at the end of which time a thick, crystalline crust forms on the bottom of the flask. This is freed, as far as possible, from the ethereal solution of the oily impurities, by filtration on a pump, the residue washed with small quantities of pure ether until perfectly colourless, and then spread on a porous plate. The white, crystalline mass thus obtained, which is almost pure hexamethylenetetracarboxylic acid, is cautiously warmed with water to about 80° until completely dissolved, and the solution filtered, and allowed to stand in a cool place for five or six days. The acid gradually separates in magnificent, colourless, glistening prisms; these are collected, washed with water, and dried on a porous plate over sulphuric acid in a vacuum. When analysed they gave the following results:—

I. 0·1661 gram substance gave 0·0720 gram H_2O and 0·2810 gram CO_2.
II. 0·1776 gram substance gave 0·0774 gram H_2O and 0·3016 gram CO_2.
III. 0·1554 gram substance gave 0·0699 gram H_2O and 0·2666 gram CO_2.

	Theory.	Found.		
	$C_{10}H_{12}O_8$.	I.	II.	III.
C........	46·15 p. c.	46·14	46·31	46·78 p. c.
H........	4·61 ,,	4·81	4·84	4·98 ,,
O........	49·23 ,,	49·05	48·85	48·24 ,,

Analysis III was made with a sample of the acid, before recrystallisation from water.

Hexamethylenetetracarboxylic acid is readily soluble in hot, and moderately in cold, water; it dissolves freely in hot alcohol, but is only very sparingly soluble in ether. When heated rapidly in a capillary tube, it decomposes at about 218—220° with evolution of carbonic anhydride and formation of a mixture of Γ^{cis} and Γ^{cistrans} hexamethylenedicarboxylic acids, as explained in the introduction.

The basicity of this acid was determined, in the first place, by titration with standard potassium hydrate solution.

1·2001 grams of the pure acid required for neutralisation 184·5 c.c.

of potassium hydrate solution (1 c.c. = 0·00559 gram KOH = 1·0313 grams KOH).

A tetrabasic acid of the formula $C_{10}H_{12}O_8$ requires for neutralisation 1·0302 gram KOH.

The *silver salt* of *hexamethylenetetracarboxylic acid*, $Ag_4C_{10}H_8O_6$, was prepared by adding a large excess of a strong solution of silver nitrate to the neutral solution of the potassium salt, prepared as above. The voluminous, white, gelatinous precipitate thus obtained was collected, washed well on a filter pump, dried first over sulphuric acid in a vacuum, then at 100°, and analysed, with the following result:—

0·3460 gram substance gave 0·0430 gram H_2O and 0·2168 gram CO_2.

0·2614 gram substance left, after ignition, 0·1630 gram Ag.

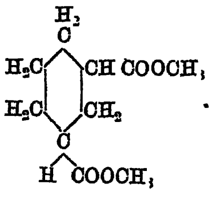
	Theory. $C_{10}H_8O_8Ag_4$.	Found.
C........	17·48 per cent.	17·09 per cent.
H........	1·17 „	1·37 „
Ag.......	62·70 „	62·32 „

The silver salt is very stable and only very slowly darkened when exposed to diffused light; it is also very sparingly soluble in water.

A dilute solution of the potassium salt of hexamethylenetetracarboxylic acid shows the following behaviour with reagents:—

Barium chloride, no precipitate in the cold, but, on heating, a white, apparently crystalline salt separates, which redissolves on cooling. *Calcium chloride* shows a similar behaviour. *Copper sulphate*, no precipitate in the cold, but, on boiling, the solution becomes intensely blue and deposits a small quantity of a light-blue precipitate. *Copper acetate* gives, in the cold, a pale-blue precipitate, which is much increased by boiling. *Lead acetate*, a white, gelatinous precipitate, sparingly soluble in water.

Methyl Hexamethylenemetadicarboxylate,



Hexamethylenetetracarboxylic acid, when heated at 200—220°, is, as has already been stated, decomposed with evolution of 2 mols. CO_2 and formation of two isomeric hexamethylenemetadicarboxylic acids.

The amount of the tetracarboxylic acid obtained as described above is small, and although the dark-coloured ethereal mother liquors still contain considerable quantities of this acid, no method could be devised by which it could readily be extracted. Fortunately, the hexamethylenedicarboxylic acids can be obtained from this crude product without further purification, the following method, which has been repeatedly employed, giving satisfactory results.

The crude, dark-brown acid which is left behind after distilling the ether from the mother liquors of the pure hexamethylenetetracarboxylic acid, and which weighed about 122 grams, was heated at 220—230° until the evolution of carbonic anhydride had ceased; the residue (73 grams) was dissolved in 4—6 times its weight of methyl alcohol, mixed with about 50 grams of concentrated sulphuric acid, and the mixture heated to boiling on a reflux apparatus for 5 hours. The product was then poured into a large volume of water, extracted four times with ether, the ethereal solution washed twice with very dilute sodium carbonate solution, dried over anhydrous potassium carbonate, evaporated, and the residual dark-brown oil (71 grams) purified by rapid fractionation under reduced pressure (60 mm.). About 28 grams distilled between 170° and 177° as a colourless oil, leaving a quantity of a dark-coloured residue of very high boiling point in the retort. On repeated fractionation, the methyl salt was obtained pure, boiling at 172—175° (60 mm.); the analysis gave the following results:—

0·1626 gram substance gave 0·1192 gram H_2O and 0·3578 gram CO_2.

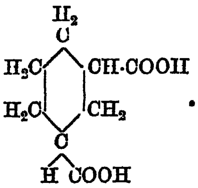
	Theory. $C_{10}H_{16}O_4$.	Found.
C........	60·00 per cent.	60·00 per cent.
H........	8·00 ,,	8·14 ,,
O........	32·00 ,,	31·86 ,,

The molecular weight of this ethereal salt was determined by Raoult's method, with the following result, using acetic acid as the solvent:—

Weight of substance taken	1·0117 gram.
Weight of acetic acid taken..............	50·21 ,,
Depression of the melting point	0·373°
Molecular weight calculated from these data	= 211
Theory for $C_{10}H_{16}O_4$	= 200

This ethereal salt is a mixture of the methyl salts of Γ^{cis} and $\Gamma^{cistrans}$ hexamethylenedicarboxylic acid. It is a colourless, fairly mobile liquid, which possesses an odour closely resembling that of the ethereal salts of the higher members of the succinic series.

Cis *Hexamethylenemetadicarboxylic Acid*,



The hydrolysis of methyl hexamethylenedicarboxylate is readily carried out by boiling the pure methyl salt with 1½ times the calculated quantity of alcoholic potash for two hours on a water-bath. The product is evaporated nearly to dryness, the residue dissolved in water, vigorously boiled until the last traces of alcohol have been expelled, and the cold alkaline solution acidified with hydrochloric acid and extracted five times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating, deposits a thick, almost colourless oil, which, on standing over sulphuric acid in a vacuum, gradually solidifies, and in about 14 days is converted into a hard cake of crystals. The crude acid thus obtained is spread on a porous plate, allowed to stand until all traces of oily impurity have been absorbed, the resulting colourless mass dissolved in boiling benzene, mixed with light petroleum (b. p. 60—70°) until a slight turbidity is noticeable, the solution again heated to boiling, and then allowed to stand in a cool place for two or three days. In this way a quantity of a hard, white, crystalline substance was obtained, which was collected, washed with cold benzene, dried on a porous plate at 80°, and analysed with the following result:—

0·1442 gram substance gave 0·0930 gram H_2O and 0·2954 gram CO_2.

	Theory. $C_8H_{12}O_4$.	Found.
C	55·81 per cent.	55·88 per cent.
H	6·98 ,,	7·16 ,,
O	37·21 ,,	36·96 ,,

This analysis agrees well with the formula of hexamethylenedicarboxylic acid, and the general behaviour of the acid, and especially the stability of its sodium salt to potassium permanganate, is in accordance with this view, but the substance is, nevertheless, not a definite compound, as the following experiment shows.

When heated in a capillary tube, the acid shows no definite melting point; the crystals begin to soften at 116°, and are not completely melted when the temperature has risen to 135°. The reason for this behaviour was found, on further investigation, to be due to the fact that the substance is a mixture of varying proportions of two isomeric acids,

$C_8H_{12}O_4$, that is, of Γ^{cis} and $\Gamma^{cistians}$ hexamethylenemetadicarboxylic acids. At first the separation of these two isomerides was accomplished by oft-repeated recrystallisation, first from benzene, then from a mixture of benzene and light petroleum, and finally from concentrated hydrochloric acid; the less soluble (Γ^{cis}) acid was found to melt at 159—161°, the more readily soluble ($\Gamma^{cistrans}$) acid at 118—120°.

Subsequently, it was discovered that the separation could be much more readily effected by taking advantage of the fact that the calcium salt of Γ^{cis} hexamethylenedicarboxylic acid is much less soluble in water than that of the $\Gamma^{cistians}$ dicarboxylic acid. The mixed acids, after one crystallisation from benzene and light petroleum, are dissolved in a considerable bulk of water, the solution heated to about 50° and agitated with a very slight excess of calcium carbonate, care being taken that enough water is present to prevent the precipitation of the sparingly soluble calcium salt of the Γ^{cis} acid. The solution is then filtered from the slight excess of calcium carbonate, and evaporated on a water-bath until a considerable crop of crystals has formed; these are collected, washed well with hot water, and the evaporation of the filtrate and subsequent separation of the crystals formed continued until only a small bulk of liquid remains.

The various crops of crystals consist of the almost pure calcium salt of Γ^{cis} hexamethylenedicarboxylic acid, the very soluble calcium salt of the isomeric acid remaining in solution.

In order to obtain the free Γ^{cis} acid, the crystals are boiled with sufficient concentrated hydrochloric acid to dissolve them, and the solution filtered through glass wool and set aside to cool slowly. The mass of needle-shaped crystals thus obtained, after washing with concentrated hydrochloric acid, recrystallising from this solvent, and drying at 100°, melted not quite sharply at 159—162°; the substance was, therefore, again converted into the calcium salt, the regenerated acid twice recrystallised from concentrated hydrochloric acid, and the beautiful, colourless crystals, which melted at 161—163°, analysed with the following result:—

I. 0·1370 gram substance gave 0·0882 gram H_2O and 0·2806 gram CO_2.

II. 0·1507 gram substance gave 0·0969 gram H_2O and 0·3081 gram CO_2.

	Theory. $C_8H_{12}O_4$.	Found. I.	 II.	
C	55·81 per cent.	55·86	55·75	per cent.
H	6 98 „	7·15	7·14	„
O	37·21 „	36·99	37 11	„

Γ^{cis} *Hexamethylenedicarboxylic acid* melts at 161—163°. It is very soluble in warm water, benzene, and alcohol, and moderately so in ether, but only sparingly in light petroleum; it crystallises well from water or benzene, but best from boiling concentrated hydrochloric acid, from which it separates rapidly on cooling, in the form of slender, colourless needles.

Generally speaking, this acid is less soluble in solvents than the isomeric $\Gamma^{cistrans}$ acid, but the difference in solubility is not sufficient to allow of the two acids being readily separated by recrystallisation. The solution of Γ^{cis} hexamethylenedicarboxylic acid in dilute carbonate of soda does not decolorise potassium permanganate even on long standing (compare Baeyer, *Annalen*, **245**, 146). The acid is, however, readily oxidised by nitric acid, although it is only slowly acted on when boiled with potassium dichromate and dilute sulphuric acid. When heated with concentrated sulphuric acid, a vigorous action sets in, with evolution of sulphurous anhydride and subsequent charring; this experiment was repeated several times in the hope that under suitable conditions isophthalic acid might be obtained, but as yet with only negative results.

The basicity of the acid was determined by titration with standard solution of potassium hydrate, using a trace of phenolphthalein as indicator.

0·2378 gram substance required for neutralisation 27·8 c.c. of potassium hydrate solution (1 c.c. = 0·00559 gram KOH) = 0·1554 gram KOH.

A bibasic acid of the formula $C_8H_{12}O_4$ requires theoretically 0·1548 gram KOH.

Salts of Γ^{cis} *Hexamethylenedicarboxylic Acid.*

Silver salt, $Ag_2C_8H_{10}O_4$.—This is thrown down on the addition of silver nitrate to the warm neutral solution of the potassium salt as a white, apparently crystalline precipitate; this is collected, washed well with water, and dried, first on a porous plate over sulphuric acid in a vacuum, and then at 100°; when analysed, it gave the following result:—

I. 0·2124 gram substance gave 0·0515 gram H_2O; 0·1925 gram CO_2, and 0·1189 gram Ag.

II. 0·1640 gram substance left on ignition 0·0912 gram Ag.

	Theory.		Found.		
	$C_8H_{10}Ag_2O_4$.		I.	II.	
C	24·92	per cent.	24·72	—	per cent.
H	2·59	„	2·69	—	„
Ag	55·87	„	55·93	55·61	„

This salt is exceedingly stable; it can be heated to 120° without apparent change, and is only very slowly darkened by exposure to diffused daylight; it is only sparingly soluble in water.

Calcium Salt, $C_8H_{10}O_4Ca + 3H_2O$ (?).—The preparation of this characteristic salt is given above (p. 809). The analysis of three different samples of the air-dried substance indicates that it crystallises with 3 mols. H_2O, two of which are given off at 100°, and the third at 180°.

I. The salt was exposed to the air for two days.
  0·1610 gram substance, heated at 100°, lost 0·0212 gram = 13·23 per cent.
II. The salt was exposed to the air for four days.
  0·1561 gram substance, heated at 100°, lost 0·0190 gram = 12·17 per cent.
III. The salt had been exposed to the air for eight days.
  0·2265 gram substance, heated at 100°, lost 0·0245 gram = 10·80 per cent.

Theoretically, the salt $C_8H_{10}O_4Ca + 3H_2O$, giving off two of its three molecules of water of crystallisation, should lose 13·63 per cent. in weight: it would therefore appear from the above numbers that a portion of the water of crystallisation is gradually given off on exposure to the air at ordinary temperature.

The residues from Experiments II and III, on heating at 175° in a Victor Meyer drying oven, heated by boiling aniline, behaved as follows:—

II. 0·1371 gram substance lost 0·0112 gram = 8·17 per cent.
III. 0·2020 gram substance lost 0·0180 gram = 8·91 per cent.

$CaC_8H_{10}O_4 + H_2O$ contains 7·99 per cent. of water of crystallisation. The analysis of the salt, dried at 175° till constant, gave the following results:—

I. 0·1259 gram substance, heated with sulphuric acid, gave 0·0792 gram $CaSO_4$.
II. 0·1392 gram substance, heated with sulphuric acid, gave 0·0878 gram $CaSO_4$.

	Theory. $CaC_8H_{10}O_4$.	Found. I.	Found. II.
Ca	19·05 per cent.	18·51	18·55 per cent.

This calcium salt crystallises in the form of slender needles, which when once deposited are only very sparingly soluble in water. A sparingly soluble calcium salt, probably identical with the above, is produced when calcium chloride is added to a strong solution of the ammonium salt of the acid, and the mixture boiled. A neutral solution of the potassium salt of Γ^{cis} hexamethylenedicarboxylic acid, of the strength obtained by neutralising the dry acid with standard potassium hydrate solution (1 c.c. = 0·00559 gram KOH), shows the following behaviour with reagents :—

Copper sulphate, a light blue precipitate, very sparingly soluble even in boiling water. *Zinc sulphate*, no precipitate in the cold, but on boiling a slight turbidity. *Lead acetate*, a white, crystalline precipitate, which forms at once, and under the microscope is seen to consist of groups of irregularly formed needles; the precipitate is almost insoluble in boiling water. *Barium* and *calcium chlorides*, no precipitate.

Anhydride of Γ^{cis} Hexamethylenedicarboxylic Acid.

In the introduction to this paper, it is stated that, in view of Baeyer's deductions from his experiments on the reduction of terephthalic acid, it might be expected that Γ^{cis} hexamethylenemetadicarboxylic acid would behave like a fatty acid of similar constitution, such as glutaric acid, and, like this acid, under suitable treatment yield an anhydride. Although, at first, this Γ^{cis} acid, on account of its high melting point and other properties, was thought to be the $\Gamma^{cis\text{-}trans}$ or fumaroid form of hexamethylenedicarboxylic acid, it nevertheless seemed possible, that, when digested with acetyl chloride, this modification might be converted into the anhydride of the Γ^{cis} acid, just as fumaric acid, under similar circumstances, yields maleic anhydride (Perkin, *Ber.*, **15**, 1073, and Anschutz, *Ber.*, **14**, 2792).

In order to test this supposition, 1 gram of the pure Γ^{cis} acid was heated in a very small flask, connected with a reflux apparatus, with excess of acetyl chloride for about one hour, the excess of acetyl chloride distilled off, and the almost colourless, oily residue transferred to a small dish and heated gently on a sand-bath till free from acetic acid. The product, which on cooling solidified to a hard mass of needle-shaped crystals, was spread on a porous plate to remove traces of oily impurity, the colourless, crystalline residue dissolved in a little boiling benzene, mixed with about an equal bulk of hot light petroleum, and allowed to cool slowly. In this way the anhydride of Γ^{cis} hexamethylenedicarboxylic acid was obtained pure in the form of magnificent, glistening, needle-shaped crystals, which, after drying at 100°, gave the following numbers on analysis :—

0·1142 gram substance gave 0·0689 gram H_2O, and 0·2604 gram CO_2.

	Theory. $C_8H_{10}O_3$.	Found.
C	62·33 per cent.	62·19 per cent.
H	6·50 ,,	6·70 ,,
O	31·17 ,,	31·11 ,,

This anhydride melts at 187—189° with slight previous softening, and distils at a high temperature almost without decomposition. It is readily soluble in benzene, acetic acid, and alcohol, excessively so in chloroform, but only sparingly in cold bisulphide of carbon and light petroleum. Hexamethylenedicarboxylic anhydride is only very slowly decomposed by cold water or cold dilute sodium carbonate solution, but it dissolves readily in hot water, and the solution, if sufficiently concentrated, deposits, on cooling, needle-shaped crystals of pure Γ^{cis} hexamethylenedicarboxylic acid (m. p. 161—163°).

Conversion of Γ^{cis} Hexamethylenedicarboxylic Acid into $\Gamma^{cistrans}$ Hexamethylenedicarboxylic Acid.

This interesting isomeric change was brought about by heating the very carefully purified Γ^{cis} acid with concentrated hydrochloric acid in a sealed tube at 180°, but as stated in the introduction the conversion is only partial, a considerable quantity of the original acid remaining unchanged. The tube, on cooling, contained a granular, crystalline mass, which melted irregularly at 135—150°, and behaved in every respect as a mixture of the Γ^{cis} and $\Gamma^{cistrans}$ acids.

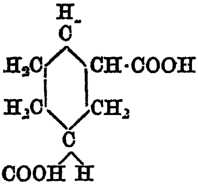
In order to prove the formation of the $\Gamma^{cistrans}$ acid, the contents of the tube was extracted four times with ether, the ethereal solution evaporated, the residue dissolved in a little water, neutralised with ammonia, heated to boiling, and gradually mixed with a large excess of a concentrated solution of calcium chloride. The heavy, white, satiny precipitate of the calcium salt of the Γ^{cis} acid thus produced was collected on a filter, washed with hot water, and decomposed with hydrochloric acid, when a quantity of a white powder was obtained, which, after recrystallisation, melted at 161—163°, and consisted of pure Γ^{cis} acid. The filtrate from the sparingly soluble calcium salt was acidified with hydrochloric acid, extracted four times with ether, the ethereal solution evaporated, the residual oil stirred with a glass rod till solid, and the solid mass spread on a porous plate to remove traces of oily impurity. In this way a white, crystalline substance was obtained, which, after two fractional crystallisations from hydrochloric acid, melted at 118—120°, and possessed all the properties of $\Gamma^{cistrans}$ hexamethylenedicarboxylic acid (see next section).

Analysis :—

0·1369 gram substance gave 0·0861 gram H_2O and 0·2789 gram CO_2.

	Theory. $C_8H_{12}O_4$.		Found	
C	55·81	per cent.	55·56	per cent.
H	6·98	,,	6·98	,,
O	37·21	,,	37·46	,,

$\Gamma^{cistrans}$ *Hexamethylenemetadicarboxylic Acid*,



The mother liquors of the sparingly soluble calcium salt of Γ^{cis} hexamethylenedicarboxylic acid (see p. 809) contain the readily soluble salt of the $\Gamma^{cistrans}$ acid, together with traces of the former salt. In order to separate the two salts as far as possible, the solutions were evaporated to a small bulk (but not to such an extent as to cause the soluble calcium salt to crystallise out), filtered from a very small quantity of a calcium salt which formed, and then evaporated to dryness. The residue was dissolved in a small quantity of boiling concentrated hydrochloric acid, the solution filtered through glass wool and vigorously stirred till a small quantity of crystals had formed, again filtered, and allowed to stand in a cool place for four hours. At the end of this time a considerable crop of crystals had separated; these were collected, washed with concentrated hydrochloric acid, recrystallised from this solvent, dried at 100°, and analysed with the following result:—

0·1344 gram substance gave 0·0863 gram H_2O and 0·2750 gram CO_2.

	Theory. $C_8H_{12}O_4$.		Found.	
C	55·81	per cent.	55·81	per cent.
H	6·98	,,	7·13	,,
O	37·21	,,	37·06	,,

When heated in a capillary tube, $\Gamma^{cistrans}$ hexamethylenedicarboxylic acid melts fairly sharply at 118—120°. It is possible that, in spite of the care taken in separating and purifying this acid, it may still contain traces of Γ^{cis} hexamethylenedicarboxylic acid, and the melting point 118—120° may therefore not be quite correct. That, at the most, only traces of the acid of higher melting point are present is shown by the fact that a strong neutral solution of the $\Gamma^{cistrans}$ acid, on the addition of calcium chloride, gives no precipitate even on continued boiling.

Γ^{cistrans} hexamethylenedicarboxylic acid resembles the Γ^{cis} acid very closely in its properties; it is, however, slightly more soluble in concentrated hydrochloric acid and other solvents than the latter acid; both acids show the same stability when treated with potassium permanganate in alkaline solution.

The basicity of the acid was determined by titration with standard potassium hydrate solution.

0 6563 gram substance required for neutralisation 76·5 c.c. of potassium hydrate solution (1 c.c. = 0·00559 gram KOH) = 0·4275 gram KOH.

A bibasic acid, $C_8H_{12}O_4$, requires for neutralisation 0·4274 gram KOH.

Salts of Γ^{cistrans} Hexamethylenedicarboxylic Acid.

Silver Salt, $Ag_2C_8H_{10}O_4$.—This salt was prepared by adding silver nitrate to the warm, neutral solution of the potassium salt. It is a heavy, white precipitate, sparingly soluble in water.

Dried at 100°, this salt gave the following numbers on analysis:—

I. 0·2366 gram substance gave 0·0562 gram H_2O, 0·2124 gram CO_2, and 0·1302 gram Ag.
II. 0·2711 gram substance left on ignition 0·1513 gram Ag.
III. 0·4114 " " 0·2301 "

	Theory.	Found.			
	$C_8H_{10}Ag_2O_4$.	I.	II.	III.	
C	24·92 p. c.	24·80	—	—	p. c.
H	2·59 "	2·66	—	—	"
Ag	55·87 "	55·69	55·81	55·93	"

This salt is very stable, and in other respects very similar to the silver salt of Γ^{cis} hexamethylenedicarboxylic acid.

A solution of the potassium salt of the strength obtained by neutralising the dry acid with standard solution of potassium hydrate (1 c.c. = 0·00559 gram KOH) shows the following behaviour with reagents:—

Copper sulphate, a light-blue precipitate sparingly soluble in water. *Zinc sulphate*, no precipitate in the cold, but, on boiling, the solution becomes slightly turbid, owing to the separation of a small quantity of a zinc salt. *Lead acetate*, at first no precipitate, but in a few seconds a beautifully crystalline lead salt separates, which under the microscope is seen to consist of minute plates; this salt is almost insoluble in water. *Barium and calcium chlorides*, no precipitates.

Action of Acetyl Chloride on $\Gamma^{cistrans}$ *Hexamethylenedicarboxylic Acid. Conversion of this Acid into* Γ^{cis} *Hexamethylenedicarboxylic Acid.*

The formation of an anhydride from Γ^{cis} hexamethylenedicarboxylic acid by the action of acetyl chloride has been described on p. 812, and, for reasons there stated, it seemed interesting to determine whether the $\Gamma^{cistrans}$ acid under similar conditions would yield *the same anhydride.*

1 gram of pure $\Gamma^{cistrans}$ acid was digested with acetyl chloride for one hour, the excess of the reagent removed by evaporation, and the residual solid, crystalline substance purified by spreading it on a porous plate and subsequently recrystallising it from a mixture of benzene and light petroleum. In this way a beautiful, colourless, crystalline substance was obtained which melted at 187—189°, and in its other properties proved to be identical with the anhydride of Γ^{cis} hexamethylenedicarboxylic acid. Analysis:—

0·1063 gram substance gave 0·0629 gram H_2O and 0·2413 gram CO_2.

	Theory. $C_8H_{10}O_3$.	Found.
C	62·33 per cent.	61·90 per cent
H	6·50 „	6·59 „
O	31·17 „	31·51 „

The yield of anhydride obtained in this experiment seemed to be quantitative As, furthermore, this anhydride when dissolved in water yields Γ^{cis} hexamethylenedicarboxylic acid, it follows that the above method can be used as a means of converting the $\Gamma^{cistrans}$ acid quantitatively into the Γ^{cis} acid, whereas the conversion by means of hydrochloric acid, as described in the next section, is always incomplete.

The anhydride which is thus obtained by the action of acetyl chloride on both isomeric hexamethylenedicarboxylic acids is characterised by an extraordinary capacity for crystallising, and this property may be made use of with great advantage as a means of purifying very crude residues of the mixed acids, from which otherwise nothing crystalline could be isolated. These residues, such as washings of beakers and filter-papers, aqueous extracts of pieces of porous plate, which have been used in the purification of the acids as described in this paper, are first treated with calcium carbonate, and roughly separated into the calcium salts of the Γ^{cis} and $\Gamma^{cistrans}$ acids;

the crude acids obtained from the calcium salts are converted into the anhydride, and this substance, which if very impure will not directly solidify, dissolved in benzene and cautiously mixed with light petroleum. On standing, the anhydride separates in long crystals, and is readily purified, except in exceptional cases, when distillation under reduced pressure and subsequent recrystallisation must be resorted to.

Conversion of $\Gamma^{cistrans}$ Hexamethylenedicarboxylic Acid into Γ^{cis} Hexamethylenedicarboxylic Acid by means of Hydrochloric Acid.

One of the most interesting facts which have been noticed in this investigation is that the two isomeric hexamethylenedicarboxylic acids, when heated with hydrochloric acid at 180°, are each to some extent converted into the other, and thus, no matter which acid you start with, the product of the reaction is sure to consist of this acid mixed with an apparently definite quantity of its isomer. The isomeric change in the case of Γ^{cis} hexamethylenedicarboxylic acid has been described on p. 813, and it is therefore only necessary to show that a similar change takes place in the case of the $\Gamma^{cistrans}$ acid. For this purpose, about 1 gram of $\Gamma^{cistrans}$ hexamethylenedicarboxylic acid (m. p. 118—120°) was heated in a sealed tube with 15 c.c. of concentrated hydrochloric acid for three hours at 180°, and the crystals which separated from the concentrated solution, on cooling, collected, washed with hydrochloric acid, and dried at 100°. These crystals melted irregularly from 140—155°, and obviously contained a small quantity of unchanged $\Gamma^{cistrans}$ acid; the experiment was therefore repeated, and the action of the hydrochloric acid continued for eight hours, but the resulting acid still showed no sharp melting point. The whole was now dissolved in ammonia solution, the excess of ammonia expelled by boiling, a strong solution of calcium chloride added to the hot solution, and the copious precipitate which formed collected, washed with water, decomposed by hydrochloric acid, and the resulting acid recrystallised from this solvent. In this way a considerable quantity of Γ^{cis} hexamethylenedicarboxylic acid was obtained which melted at 159—161°, and gave the following results on analysis:—

0·1222 gram substance gave 0·0785 gram H_2O and 0·2497 gram CO_2.

	Theory. $C_8H_{12}O_4$.	Found.
C	55·81 per cent.	55·73 per cent.
H	6·98 „	7·03 „
O	37·21 „	37·24 „

As nearly as could be judged in a small experiment, about 60 per cent. of the Γ^{cistrans} acid is converted into the Γ^{cis} acid by this treatment. At the same time it should be mentioned that the unchanged acid was not isolated and analysed, but only roughly identified as such.

Heriot Watt College, Edinburgh.

LXXVII.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

Synthesis of Homologues of Pentanetetracarboxylic Acid and of Pimelic Acid.

By W. H. PERKIN, Jun., Ph.D., F.R.S., and BERTRAM PRENTICE.

IN a previous communication to the Society on derivatives of pentamethylene (Trans., 1887, 51, 240), it was shown that ethyl pentanetetracarboxylate, $(COOC_2H_5)_2CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(COOC_2H_5)_2$, produced by the action of trimethylene bromide on the sodium derivative of ethyl malonate, was capable of forming a disodium compound, $(COOC_2H_5)_2CNa\cdot CH_2\cdot CH_2\cdot CH_2\cdot CNa(COOC_2H_5)_2$, which, when treated with bromine, yielded ethyl pentamethylenetetracarboxylate.

This disodium compound reacts readily also with methylene iodide, forming, among other products, ethyl hexamethylenetetracarboxylate, as is shown in the preceding paper.

In the course of these experiments, it appeared to us interesting to include the study of the action of alkyl iodides on the disodium compound of ethyl pentanetetracarboxylate, and as a result we find that this reaction serves as a very convenient method of preparing *αα*-disubstituted pentanetetracarboxylic acid derivatives, and, indirectly, of *αα*-disubstituted pimelic acids, thus:—

$$(COOC_2H_5)_2CNa\cdot CH_2\cdot CH_2\cdot CH_2\cdot CNa(COOC_2H_5)_2 + 2RI = \\ (COOC_2H_5)_2CR\cdot CH_2\cdot CH_2\cdot CH_2\cdot CR(COOC_2H_5)_2 + 2NaI.$$

On hydrolysis, the ethereal salts thus obtained yield the corresponding tetrabasic acids, and these, when heated at 200—220°, are readily decomposed with evolution of 2 mols. of carbonic anhydride and formation of homologues of pimelic acid, thus:—

$$(COOH)_2CR\cdot CH_2\cdot CH_2\cdot CH_2\cdot CR(COOH)_2 = \\ COOH\cdot CHR\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHR\cdot COOH + 2CO_2.$$

On the other hand, it was not found possible to prepare monalkyl derivatives of pentanetetracarboxylic acid by treating ethyl pentanetetracarboxylate with 1 mol. of sodium ethylate and alkyl haloïds.

Thus, when benzyl chloride was employed, the product of the reaction was found to consist of ethyl dibenzylpentanetetracarboxylate, one half of the ethyl pentanetetracarboxylate being recovered as such. In order to explain this curious reaction, one must either suppose that ethyl pentanetetracarboxylate is incapable of forming a monosodium compound, under the conditions employed, or that the decomposition of the monosodium compound takes place thus :—

$$\text{I. } (COOC_2H_5)_2CNa\cdot[CH_2]_3\cdot CH(COOC_2H_5)_2 + C_7H_7Cl = (COOC_2H_5)_2C(C_7H_7)\cdot[CH_2]_3\cdot CH(COOC_2H_5)_2 + NaCl.$$

$$\text{II. } (COOC_2H_5)_2C(C_7H_7)\cdot[CH_2]_3\cdot CH(COOC_2H_5)_2 + (COOC_2H_5)_2CNa\cdot[CH_2]_3\cdot CH(COOC_2H_5)_2 = (COOC_2H_5)_2C(C_7H_7)\cdot[CH_2]_3\cdot CNa(COOC_2H_5)_2 + (COOC_2H_5)_2CH\cdot[CH_2]_3\cdot CH(COOC_2H_5)_2.$$

$$\text{III. } (COOC_2H_5)_2C(C_7H_7)\cdot[CH_2]_3\cdot CNa(COOC_2H_5)_2 + C_7H_7Cl = (COOC_2H_5)_2C(C_7H_7)\cdot[CH_2]_3\cdot C(C_7H_7)(COOC_2H_5)_2 + NaCl.$$

Similar results were obtained by Guthzeit and Dressel (*Annalen*, **256**, 180 and 188), who found that ethyl dicarboxyglutarate, $(COOC_2H_5)_2CH\cdot CH_2\cdot CH(COOC_2H_5)_2$, was apparently not capable of yielding a monosodium compound, and that, consequently, when the ethereal salt was treated with 1 mol. of sodium ethylate and ethyl iodide, instead of ethyl *mon*ethyldicarboxyglutarate, a mixture of ethyl *di*ethyldicarboxyglutarate with unchanged ethyl dicarboxyglutarate resulted.

Derivatives of ethyl pentanetetracarboxylate and of pimelic acid, identical with those obtained by the above method, may be conveniently prepared by acting on the sodium compound of the ethyl alkylmalonate with trimethylene bromide, thus :—

$$2(COOC_2H_5)_2CRNa + C_3H_6Br_2 = (COOC_2H_5)_2CR\cdot[CH_2]_3\cdot CR(COOC_2H_5)_2 + 2NaBr.$$

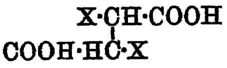
The action of trimethylene bromide on the sodium compound of ethyl isobutylmalonate was carefully investigated, and it was found that nearly 50 per cent. of the theoretical yield of ethyl diisobutylpentanetetracarboxylate was obtained in this way; hence this method may, obviously, in many cases, be conveniently employed instead of that just described, especially as it is more expeditiously carried out.

The smallness of the yield of ethyl diisobutylpentanetetracarboxylate appears to be due to a secondary reaction, in which ethyl isobutylallylmalonate is formed, with regeneration of some ethyl isobutylmalonate, thus:—

$$2(COOC_2H_5)_2CNa{\cdot}C_4H_9 + C_3H_6Br_2 =$$
$$(COOC_2H_5)_2C(CH_2{\cdot}CH{:}CH_2){\cdot}C_4H_9 + (COOC_2H_5)_2CH{\cdot}C_4H_9 + 2NaBr.$$

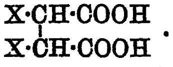
The study of the disubstituted pimelic acids is of considerable interest in view of the work lately done by Zelinsky, Auwers and Victor Meyer, Bischoff, and his collaborateurs, and others, on the stereochemical isomerism of *αα*-disubstituted acids in the succinic, glutaric, and adipic series.

The symmetrical disubstituted succinic acids, $\begin{array}{l}CHX{\cdot}COOH\\ |\\ CHX{\cdot}COOH\end{array}$, exist in two modifications or so-called stereochemical isomerides which may be conveniently represented thus:—



$$\begin{array}{r}X{\cdot}CH{\cdot}COOH\\ |\\ COOH{\cdot}HC{\cdot}X\end{array}.$$

(Fumaroïd form.)



$$\begin{array}{l}X{\cdot}CH{\cdot}COOH\\ |\\ X{\cdot}CH{\cdot}COOH\end{array}.$$

(Maleïnoïd form.)

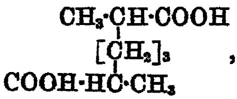
Similarly, symmetrical dimethylglutaric acid,

$$CH_2{<}\begin{array}{l}CH(CH_3){\cdot}COOH\\ CH(CH_3){\cdot}COOH\end{array},$$

exists in two modifications; the corresponding diphenylglutaric acid has, on the contrary, only been obtained in one form.

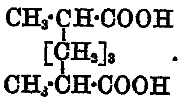
Again, symmetrical dimethyladipic acid, $\begin{array}{l}CH_2{\cdot}CH(CH_3){\cdot}COOH\\ |\\ CH_2{\cdot}CH(CH_3){\cdot}COOH\end{array}$, exists in the form of two stereochemical isomerides.

It naturally appeared to us interesting to determine whether the symmetrical *αα*-pimelic acids existed in two modifications, which, in the case of dimethylpimelic acid, would be represented by the formulæ



$$\begin{array}{r}CH_3{\cdot}CH{\cdot}COOH\\ |\\ [CH_2]_3\\ |\\ COOH{\cdot}HC{\cdot}CH_3\end{array},$$

(Fumaroïd form.)



$$\begin{array}{l}CH_3{\cdot}CH{\cdot}COOH\\ |\\ [CH_2]_3\\ |\\ CH_3{\cdot}CH{\cdot}COOH\end{array}.$$

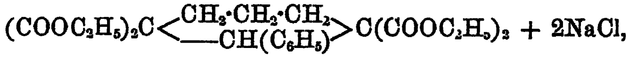
(Maleïnoïd form.)

With this object in view, a considerable number of these di-substituted pimelic acids were prepared, and very carefully fractionally recrystallised from water, but in no case could a separation into two isomerides be accomplished. This investigation was, however, rendered very difficult from the fact that, unlike the disubstituted succinic acids, the acids of the pimelic series have little capacity for crystallising.

It was frequently noticed that the melting points of the acids were not so sharp as could have been desired, and there is, therefore, still a possibility that stereochemical isomerides exist, which, however, are so similar in properties that means other than simple recrystallisation would need to be resorted to in order to effect separation.

A curious result was obtained in studying the action of benzal chloride on the disodium compound of ethyl pentanetetracarboxylate. This experiment was instituted in the hope of obtaining phenylhexamethylene derivatives, thus:—

$$(COOC_2H_5)_2CNa\cdot[CH_2]_3\cdot CNa(COOC_2H_5)_2 + C_6H_5\cdot CHCl_2 =$$



$$(COOC_2H_5)_2C{<}\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ \text{——}CH(C_6H_5)\end{matrix}{>}C(COOC_2H_5)_2 + 2NaCl,$$

a reaction analogous to the formation of ethyl hexamethylenetetracarboxylate by the action of methylene iodide on the disodium compound of ethyl pentanetetracarboxylate (compare p. 803).

On hydrolysing the ethereal salt obtained in this reaction, a hexamethylenetetracarboxylic acid was not obtained, as was expected, but instead of this, an acid which on investigation proved to be dibenzalpimelic acid. The formation of this acid by the action of benzal chloride on the disodium compound of ethyl pentanetetracarboxylate and subsequent hydrolysis may be represented thus:—

$$2(COOC_2H_5)_2CNa\cdot[CH_2]_3\cdot CNa(COOC_2H_5)_2 + 2C_6H_5\cdot CHCl_2 + 10KOH$$
$$= COOK\cdot C(:CH\cdot C_6H_5)\cdot[CH_2]_3\cdot C(:CH\cdot C_6H_5)\cdot COOK +$$
$$(COOK)_2CH\cdot[CH_2]_3\cdot CH(COOK)_2 + 4NaCl + 8C_2H_5\cdot OH + 2K_2CO_3,$$

but the exact course of the reaction is difficult to explain.

It is, however, possible that, in the first place, an intermediate compound,

$$(COOC_2H_5)_2C(CHCl\cdot C_6H_5)\cdot[CH_2]_3\cdot C(CHCl\cdot C_6H_5)(COOC_2H_5)_2,$$

is formed, half of the sodium compound of ethyl pentanetetracarboxylate remaining unacted on. On subsequent hydrolysis, this intermediate substance would yield dibenzalpimelic acid, thus:—

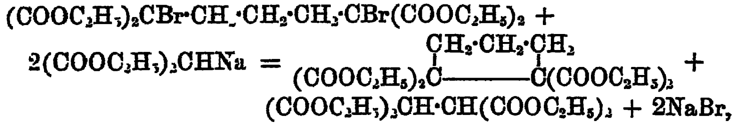
$$(COOC_2H_5)_2(CHCl\cdot C_6H_5)C\cdot[CH_2]_3\cdot C(CHCl\cdot C_6H_5)(COOC_2H_5)_2 +$$
$$8KOH = COOK\cdot C(CH\cdot C_6H_5)\cdot[CH_2]_3\cdot C(CH\cdot C_6H_5)\cdot COOK +$$
$$2KCl + 4C_2H_5\cdot OH + 2K_2CO_3 + 2H_2O,$$

whilst the excess of ethyl pentanetetracarboxylate, on hydrolysis and subsequent heating at 200°, would yield pimelic acid; this was actually found as one of the products of the reaction.

Ethyl pentanetetracarboxylate is readily acted on by bromine with formation of ethyl $\alpha\alpha$-dibromopentanetetracarboxylate and evolution of hydrogen bromide, thus:—

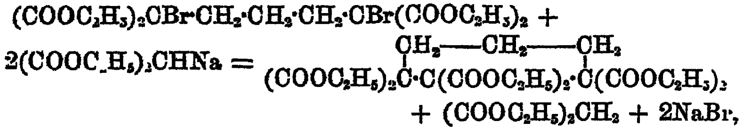
$$(COOC_2H_5)_2CH\cdot[CH_2]_3\cdot CH(COOC_2H_5)_2 + 2Br_2 = (COOC_2H_5)_2CBr\cdot[CH_2]_3\cdot CBr(COOC_2H_5)_2 + 2HBr.$$

This dibromo-compound is remarkable for the ease with which it is converted into ethyl pentamethylenetetracarboxylate, this change taking place when the substance is treated with alcoholic potash or alcoholic ammonia, and apparently quantitatively when it is boiled in alcoholic solution with the sodium compound of ethyl malonate. It seems probable that this latter reaction takes place according to the equation



$$\begin{array}{l}(COOC_2H_5)_2CBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CBr(COOC_2H_5)_2 + \\ 2(COOC_2H_5)_2CHNa = \begin{array}{c}CH_2\cdot CH_2\cdot CH_2 \\ (COOC_2H_5)_2C\text{———}C(COOC_2H_5)_2\end{array} + \\ \qquad (COOC_2H_5)_2CH\cdot CH(COOC_2H_5)_2 + 2NaBr,\end{array}$$

a striking example of the tendency towards the formation of a pentamethylene ring; clearly by this reaction a hexamethylene ring might have been produced, thus:—



$$\begin{array}{l}(COOC_2H_5)_2CBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CBr(COOC_2H_5)_2 + \\ 2(COOC_2H_5)_2CHNa = \begin{array}{c}CH_2\text{——}CH_2\text{——}CH_2 \\ (COOC_2H_5)_2C\cdot C(COOC_2H_5)_2\cdot C(COOC_2H_5)_2\end{array} \\ \qquad + (COOC_2H_5)_2CH_2 + 2NaBr,\end{array}$$

and it would be a matter of considerable interest to determine whether by varying the conditions the hexamethylene compound could be obtained.

With regard to the descriptions of the properties of the substances obtained in this research, we wish to add that the density and magnetic rotation determinations were made by W. H. Perkin (sen.), who will, in a forthcoming paper, describe his observations in detail. We have also to express our thanks to Dr. J. Walker, to whom we are indebted for the determinations of the dissociation constants for the electrical conductivity of the pimelic acids.

Ethyl Pentanetetracarboxylate,

$(COOC_2H_5)_2CH\cdot[CH_2]_3\cdot CH(COOC_2H_5)_2$.

This substance has already been described (Trans., 1887, 41, 240).

In preparing large quantities of this ethereal salt, the following quantities are advantageously employed in one operation:—

Ethyl malonate	320 grams.
Trimethylene bromide	210 ,,
Sodium	46 ,,
Alcohol	500—550 grams.

The reaction which sets in after mixing these substances (Trans., **41**, 241) is at times very violent; it is, therefore, necessary to employ a large flask fitted with a long condenser, and resting on several folds of cloth, otherwise loss from frothing or from breakage due to bumping may result. The crude ethyl pentanetetracarboxylate obtained from the product of this reaction by the method previously recommended (*loc. cit.*) does not boil constantly; but it nevertheless appears to be a very fairly pure substance, and for synthetical purposes the fraction passing over between 255° and 275° (under a pressure of 100 mm.) was found to give excellent results. A sample of this ethereal salt boiling at 230—235° (30 mm.)* gave on analysis the following numbers—

0·1705 gram substance gave 0·1198 gram H_2O and 0·3350 gram CO_2.

	Theory. $C_{17}H_{28}O_8$.	Found.
C	56·67 per cent.	56·78 per cent.
H	7·78 ,,	7·81 ,,
O	35·55 ,,	35·41 ,,

The boiling point of this ethereal salt was previously given as 259—262° (100 mm.), and this agrees well with that given above, that is, 230—235° (30 mm.).

Records of the yields obtained in a large number of experiments on the action of trimethylene bromide on the sodium compound of ethyl malonate have been kept, and the following may be given as approximately representing the proportion of the various products obtained from 1 kilo. of ethyl malonate.

Crude product of the reaction		1050—1090 grams.
After distillation in steam	crude ethyl tetramethylenedicarboxylate	570—620 ,,
	crude ethyl pentanetetracarboxylate	420—470 ,,
Ethyl pentanetetracarboxylate, b. p. 255—275° (100 mm.)		360—390 ,,

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* All boiling points given in this paper are to be understood as being taken with the thread of the thermometer immersed entirely in the vapour of the boiling liquid.

Pentanetetracarboxylic Acid, $(COOH)_2CH\cdot[CH_2]_3\cdot CH(COOH)_2$.

In the previous communication (*loc. cit.*), this acid was only obtained in a crude state, and was not then examined and analysed; it may be prepared in an approximately pure state in the following way:—

9 grams of the pure ethereal salt are gradually added to a moderately concentrated solution of 10 grams of pure potassium hydrate in methyl alcohol, and the mixture heated to boiling in a reflux apparatus for two hours. The product is evaporated, mixed with water, again evaporated to a small bulk to remove the last traces of alcohol, acidified with dilute sulphuric acid, and extracted at least 20 times with pure ether which must be quite free from alcohol. The ethereal solution is very carefully dried over calcium chloride, filtered, evaporated, and the residual oily acid allowed to stand several days over sulphuric acid in a vacuum.

In this way a crystalline cake is obtained, which after being freed, as far as possible, from oily mother liquor by spreading on a porous plate, is washed rapidly with a small quantity of pure ether on a piece of porous tile, and the residual white, crystalline mass dried over sulphuric acid in a vacuum. When analysed, it gave the following result:—

0·1396 gram substance gave 0·0667 gram H_2O and 0·2239 gram CO_2.

	Theory. $C_9H_{12}O_8$.	Found.
C	43·55 per cent.	43·74 per cent.
H.......	4·84 „	5·30 „
O.......	51·61 „	50·96 „

Pentanetetracarboxylic acid begins to melt at 125—130°, and gradually decomposes with evolution of carbonic anhydride and formation of pimelic acid, thus:—

$$(COOH)_2CH\cdot[CH_2]_3\cdot CH(COOH)_2 = 2CO_2 + COOH\cdot CH_2\cdot[CH_2]_3\cdot CH_2\cdot COOH.$$

It is excessively soluble in water or alcohol, readily in ether, but almost insoluble in benzene and light petroleum.

The basicity of the acid was determined by titrating a known quantity with standard potassium hydrate solution.

0·5662 gram acid required for neutralisation 88·5 c.c. of standard solution of potassium hydrate (1 c.c. = 0·00559 gram KOH) = 0·492 gram KOH.

A tetrabasic acid of the formula $C_9H_{12}O_8$ requires = 0·511 gram KOH.

The results of the analysis and the titration of this acid seem to show that it contains a small quantity of pentanetricarboxylic acid.

Preparation of Ethyl Pimelate and Pimelic Acid.

The fact that pentanetetracarboxylic acid, on heating, is decomposed into pimelic acid and carbonic anhydride affords a valuable method for the preparation of this acid: more especially as other methods of preparation leave some doubt as to the normal structure of the resulting acid. We have had occasion to prepare a quantity of pimelic acid, and have found the following method, which differs from that previously given (Trans., 1887, **51**, 242), to give admirable results:—

Crude ethyl pentanetetracarboxylate (which need not be submitted to fractionation in a vacuum) is hydrolysed by boiling with an alcoholic solution of 1½ times the theoretical quantity of potassium hydrate for 2 to 3 hours in a reflux apparatus, the alcohol driven off on a water-bath, and the residue dissolved in water and boiled vigorously to remove the last traces of alcohol. The concentrated solution is acidified with an excess of dilute sulphuric acid, and extracted about 20 times with pure ether; the extract is then dried over calcium chloride. evaporated, and the residual crude pentanetetracarboxylic acid heated in an oil-bath at about 200—220° until the evolution of carbonic anhydride has ceased. The crude, dark-coloured pimelic acid thus obtained is best purified by conversion into its ethereal salt; for this purpose, the crude product is dissolved in about 6 times its weight of absolute alcohol, about one-fifth of the volume of concentrated sulphuric acid added, and the whole heated to boiling in a reflux apparatus for two hours. The alcoholic solution is then poured into much water, extracted four times with ether, and the ethereal solution washed twice with water and once with dilute sodium carbonate solution; the ethereal solution, after being dried over potassium carbonate, is evaporated, and the residual, brownish-coloured oil purified by distillation under reduced pressure (100 mm.). After two fractionations, nearly the whole of it passed over between 192° and 194° (under a pressure of 100 mm.), and gave, on analysis, the following numbers:—

0·1054 gram substance gave 0·0891 gram H_2O and 0·2360 gram CO_2.

	Theory. $COOC_2H_5·[CH_2]_5·COOC_2H_5$	Found
C	61·11 per cent	61·06 per cent.
H	9·26 „	9·38 „
O	29·63 „	29·46 „

Ethyl pimelate is a colourless, limpid oil, which has a penetrating odour, somewhat resembling that of ethyl succinate. The density of this ethereal salt was found to be *d* 4°/4° = 1·0080; *d* 15°/15° = 0·9988; *d* 25°/25° = 0·9920.

The magnetic rotation determinations gave—

t.	Sp. rotation.	Mol rotation.
18·9°	0·9481	11·424

The acid was obtained from the ethereal salt by digesting it with excess of alcoholic potassium hydrate, evaporating the solution with the addition of water until free from alcohol, acidifying with dilute sulphuric acid, and extracting several times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a colourless oil which soon solidified to a hard, crystalline cake of almost pure pimelic acid; this was readily purified by conversion into the characteristic calcium salt (Dale, Schorlemmer, *Annalen*, **199**, 147) and subsequent recrystallisation from benzene. The beautiful product thus obtained gave on analysis:—

0·1202 gram substance gave 0·0828 gram H_2O and 0·2313 gram CO_2.

	Theory. $COOH·[CH_2]_5·COOH$	Found.
C	52·50 per cent	52·48 per cent.
H	7·50 „	7·65 „
O	40·00 „	39·87 „

The yield of pure pimelic acid obtained in this way from 180 grams of crude ethyl pentanetetracarboxylate was about 47 grams; the theoretical being 80 grams.

In a subsequent experiment made with the pure ethereal salt, the yield of recrystallised acid obtained was over 80 per cent. of the theory. The dissociation constant for the electrical conductivity of pimelic acid at different concentrations is K = 0·00341 (Ostwald gives 0·00357).

Pimelic acid is readily soluble in water.* 100 parts of water dissolve about 2·52 parts of pimelic acid at 13·5°.

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* The determinations of the solubility of pimelic acid and its homologues which are given in this paper were made simultaneously; the acids were dissolved in

Ethyl Dibromopentanetetracarboxylate,
$(COOC_2H_5)_2CBr\cdot[CH_2]_3\cdot CBr(COOC_2H_5)_2$.

Ethyl pentanetetracarboxylate is very readily attacked by bromine at ordinary temperatures, and. if the addition of bromine is continued as long as decolorisation takes place, ethyl dibromopentanetetracarboxylate is formed, thus:—

$$(COOC_2H_5)_2CH\cdot[CH_2]_3\cdot CH(COOC_2H_5)_2 + 2Br_2 =$$
$$(COOC_2H_5)_2CBr\cdot[CH_2]_3\cdot CBr(COOC_2H_5)_2 + 2HB$$

The following method answers well for preparing considerable quantities of this substance:—

36 grams of pure ethyl pentanetetracarboxylate is dissolved in 100 grams of pure dry chloroform, and 32 grams of bromine added very slowly and drop by drop through a dropping funnel; the mixture should be cooled during the operation by a stream of water, although the rise of temperature due to the reaction is not considerable. Each drop of bromine, as it comes in contact with the solution of the ethereal salt, is instantly decolorised, until about 28—30 grams have been added; then the reaction becomes very slow, and the liquid does not become colourless even on long standing.

The product thus obtained is washed twice with water, then with dilute sodium hydrate solution, and again with water; after being dried over calcium chloride, the chloroform is removed by allowing the solution to evaporate at a gentle heat on a water-bath, the last traces of chloroform being expelled by a current of air. The thick, oily residue, on cooling, soon begins to solidify, and if the crystallisation takes place slowly, large, well-formed, four-sided, tabular crystals, with bevelled edges, separate, and continue to grow until the whole mass has become solid. This crystalline mass was carefully pressed, dried over sulphuric acid in a vacuum, and analysed with the following result:—

0·1501 gram substance gave 0·0736 gram H_2O and 0·2140 gram CO_2.

0·2331 gram substance, heated with nitric acid and nitrate of silver in a sealed tube, gave 0·1684 gram AgBr.

	Theory. $C_{17}H_{26}Br_2O_8$.	Found.
C	39·38 per cent.	39·48 per cent.
H.......	5·02 „	5·44 „
Br	30·89 „	31·15 „

warm water, the solutions allowed to stand for two days to crystallise, filtered, and the amount of acid contained in the solutions estimated by titration.

Ethyl dibromopentanetetracarboxylate melts at about 38—40°. It is very readily soluble in most organic solvents; in cold light petroleum, however, it is only moderately soluble. We were not successful in our attempts to recrystallise the substance from any of these solvents.

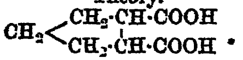
Ethyl dibromopentanetetracarboxylate is readily hydrolysed by boiling with a mixture of dilute sulphuric acid and acetic acid, with formation of a crystalline acid, which appears to be dibromopentanetetracarboxylic acid. Alcoholic potash converts the dibromo-ethereal salt into pentamethylenetetracarboxylic acid. and the same remarkable change takes place, at all events to a small extent, when the ethereal salt is heated with alcoholic ammonia in a sealed tube. Similar results were obtained in experimenting on the action of ethyl dibromopentanetetracarboxylate on the sodium compound of ethyl malonate.

It seemed possible that this reaction might lead to a synthesis of hexamethylene derivatives (as explained in the introduction), and in order to submit this view to the test of experiment we proceeded as follows:—

3·3 grams of sodium was dissolved in 35 grams of absolute alcohol, the solution of sodium ethylate thus formed diluted with 50 c.c. of pure dry ether, and then 11·5 grams of ethyl malonate and 37 grams of ethyl dibromopentanetetracarboxylate added. After standing for half an hour, the product, which was quite neutral, was mixed with water, extracted two or three times with ether, the ethereal solution evaporated, and the residual thick oil hydrolysed by boiling it in a reflux apparatus for two days, with a mixture of 1 vol. of concentrated sulphuric acid, 1 vol. of water, and 2 vols. of glacial acetic acid. Steam was then blown through the mixture until all traces of acetic acid had been expelled, the slightly brownish liquid was filtered, allowed to stand for 24 hours, and the crystalline precipitate which had formed collected, washed with water, and recrystallised twice from this solvent.

Thus purified, the acid melted at 160°, and consisted of pure pentamethylenedicarboxylic acid. Analysis gave the following result:—

0·1510 gram substance gave 0·0868 gram H_2O and 0·2952 gram CO_2.



$CH_2<\begin{array}{l}CH_2\cdot CH\cdot COOH\\ CH_2\cdot CH\cdot COOH\end{array}$

	Theory.	Found.
C	53·16 per cent.	53·31 per cent.
H	6·33 „	6·38 „
O	40·51 „	40·31 „

The yield of the acid obtained in this experiment was very large, and this method of preparation may possibly prove to be the simplest means of obtaining large quantities of pentamethylenedicarboxylic acid. Further experiments on this subject are in progress.

Ethyl Dimethylpentanetetracarboxylate, $(COOC_2H_5)_2C(CH_3)\cdot[CH_2]_3\cdot C(CH_3)(COOC_2H_5)_2$.

As the methods employed in preparing the various homologues of ethyl pentanetetracarboxylate were in all cases very similar, we propose to give one example in full, and then in the other preparations simply to refer to this, giving only such important details as may be necessary.

In preparing ethyl dimethylpentanetetracarboxylate, 4·6 grams of sodium was dissolved in 50—55 grams of absolute alcohol, the well-cooled solution mixed with 36 grams of ethyl pentanetetracarboxylate (b. p. 255—275° at 100 mm.), and then an excess of methyl iodide (35 grams) added. The latter must be cautiously added, and with constant cooling, otherwise the reaction is apt to become very violent, and loss by boiling over may occur. The mixture was transferred to a soda-water bottle, heated in a water-bath at 100° for an hour, the product mixed with water, and the oily layer which separated extracted three times with ether. The ethereal solution was well washed with water, dried over calcium chloride, evaporated, and the almost colourless, oily residue purified by fractionation under reduced pressure (30 mm.). Almost the whole distilled between 235° and 245°, and on refractionation the ethereal salt was readily obtained pure as a thick oil boiling constantly at 238—240° (30 mm.).

The analysis gave the following result:—

0·1930 gram substance gave 0·1450 gram H_2O and 0·4148 gram CO_2.

	Theory. $C_{19}H_{32}O_8$.	Found.
C	58·76 per cent.	58·61 per cent.
H	8·25 ,,	8·34 ,,
O	32·99 ,,	33·05 ,,

Ethyl dimethylpentanetetracarboxylate is a thick, colourless oil possessing a feebly ethereal odour, and boiling constantly at 238—240° (30 mm.). It is insoluble in water, but miscible with alcohol, ether, and most organic solvents.

Dimethylpentanetetracarboxylic Acid, $(COOH)_2C(CH_3)\cdot[CH_2]_3\cdot C(CH_3)(COOH)_2$.

In order to prepare this acid, the pure ethereal salt (1 mol.) was digested with an excess of a solution of pure potassium hydrate (6 mols.) in methyl alcohol for two hours in a flask connected with a reflux apparatus. The product was evaporated nearly to dryness, mixed with a considerable quantity of water, the solution again evaporated to a small bulk to remove the last traces of alcohol, acidified with dilute sulphuric acid, and extracted about 10 times with pure ether. The ethereal solution, after drying over calcium chloride, deposits during evaporation a white, sandy precipitate which consists of pure dimethylpentanetetracarboxylic acid. This was collected, washed with ether till quite colourless, dried over sulphuric acid in a vacuum, and analysed with the following results:—

I. 0·1555 gram substance gave 0·0830 gram H_2O and 0·2742 gram CO_2.

II. 0·1520 gram substance gave 0·0826 gram H_2O and 0·2698 gram CO_2.

	Theory. $C_{11}H_{16}O_8$.	Found. I.	Found. II.	
C........	47·83 per cent.	48·09	48·40	per cent.
H.......	5·79 „	5·93	6·03	„
O........	46·37 „	45·98	45·57	„

The ethereal mother liquors from this acid on evaporation deposit a less pure acid, which was used in the subsequent preparation of dimethylpimelic acid.

Dimethylpentanetetracarboxylic acid, when rapidly heated, decomposes at about 200—205° into carbonic anhydride and dimethylpimelic acid. It is very soluble in water and alcohol, sparingly so in ether, benzene, light petroleum, chloroform, and ethyl acetate. Its aqueous solution has a strongly acid reaction. The basicity of the acid was determined by titration with standard potassium hydrate solution.

0·1590 gram substance required for neutralisation 0·1285 gram KOH.

A tetrabasic acid of the formula $C_{11}H_{16}O_8$ requires 0·1289 gram KOH.

Ethyl Dimethylpimelate and Dimethylpimelic Acid,

$COOH{\cdot}CH(CH_3){\cdot}[CH_2]_3{\cdot}CH(CH_3){\cdot}COOH$.

When heated at 200°, dimethylpentanetetracarboxylic acid is rapidly decomposed with evolution of carbonic anhydride and formation of dimethylpimelic acid :—

$$(COOH)_2C(CH_3){\cdot}[CH_2]_3{\cdot}C(CH_3)(COOH)_2 = COOH{\cdot}CH(CH_3){\cdot}[CH_2]_3{\cdot}CH(CH_3){\cdot}COOH + 2CO_2.$$

The preparation and purification of this acid is readily accomplished in the following way :—

The crude tetrabasic acid, obtained as described in the previous section, is gradually heated in an oil-bath to 200°, and kept at this temperature until the evolution of carbonic anhydride ceases, the temperature being ultimately raised to 220° for one or two minutes. The crude, brownish-coloured acid is dissolved in absolute alcohol, digested with sulphuric acid, and thus converted into the diethyl salt, which is isolated and purified exactly as described under ethyl pimelate (p. 825).

Ethyl dimethylpimelate boils constantly at 195—196° (100 mm.), and in its properties closely resembles ethyl pimelate.

The analysis gave the following numbers :—

I. 0·1438 gram substance gave 0·1288 gram H_2O and 0·3352 gram CO_2.

II. 0·1270 gram substance gave 0·1132 gram H_2O and 0·2974 gram CO_2.

	Theory. $C_{13}H_{24}O_4$.	Found. I.	Found. II.
C	63·93 per cent.	63·85	63·86 per cent.
H	9·83 „	9·95	9 90 „
O	26·24 „	26·20	26·24 „

The specific gravity of ethyl dimethylpimelate is *d* 4°/4° = 0·9817 ; *d* 15°/15° = 0·9728; *d* 25°/25° = 0·9663.

The magnetic rotation determinations gave as an average—

t.	Sp. rotation.	Mol. rotation.
17·6°	0·9526	13·298

This ethereal salt is identical with the ethyl dimethylpimelate obtained by Kipping and Mackenzie (this vol., p. 571) by the action of trimethylene bromide on the sodium compound of ethyl methylacetoacetate. The boiling point given by these authors (190—191° under a pressure of 80 mm.) agrees well with that observed by us.

The preparation of *dimethylpimelic acid* from its ethereal salt is exactly similar to the preparation of pimelic acid from ethyl pimelate (p. 826).

The ethereal solution of the acid, on evaporation, deposited a thick oil which solidified when allowed to stand over sulphuric acid in a vacuum. The crystalline cake thus obtained was strongly pressed, and then purified by recrystallisation from water. This operation can be successfully carried out by dissolving the acid in sufficient hot water to allow of only a small quantity of oil separating on cooling. After standing for some days, beautiful, glistening, prismatic crystals grew from the oily drops; these were collected, washed with a little water, dried first on a piece of porous plate over sulphuric acid in a vacuum, then at 50—60°, and analysed (I). The mother liquors from these crystals, on standing over sulphuric acid in a vacuum, gradually deposited magnificent, glistening prisms, arranged in stellate groups: these were also collected and analysed (II).

I. 0·1460 gram substance gave 0·1132 gram H_2O and 0·3062 gram CO_2.

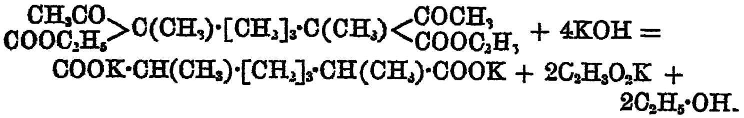
II. 0·1453 gram substance gave 0·1157 gram H_2O and 0·3060 gram CO_2.

	Theory.	Found.	
	$C_9H_{16}O_4$.	I.	II.
C	57·44 per cent.	57·19	57·43 per cent.
H	8·51 ,,	8·61	8·84 ,,
O	34·05 ,,	34·20	33·73 ,,

Dimethylpimelic acid melts at 74—76°.

The dissociation constant for the electrical conductivity of this acid at different concentrations is K = 0·00337.

Dimethylpimelic acid has already been obtained by Kipping and Mackenzie (this vol., p. 570), by the hydrolysis of ethyl dimethyldiacetylpimelate, thus:—



$$\begin{matrix}CH_3CO\\COOC_2H_5\end{matrix}\!>C(CH_3)\cdot[CH_2]_3\cdot C(CH_3)<\!\begin{matrix}COCH_3\\COOC_2H_5\end{matrix} + 4KOH =$$
$$COOK\cdot CH(CH_3)\cdot[CH_2]_3\cdot CH(CH_3)\cdot COOK + 2C_2H_3O_2K + 2C_2H_5\cdot OH.$$

These authors recrystallised their acid from a mixture of benzene and light petroleum, and obtained crystals melting at 81°.

We have also repeatedly recrystallised our acid from these solvents, but have never been able to observe a higher melting point than 74—76°.

Dimethylpimelic acid is readily soluble in water; 100 parts of water at 13·5° dissolve about 2·19 parts of the pure acid; but this number must be regarded as approximate only, since this acid does not crystallise from water so readily as the other pimelic acids.

Ethyl Diethylpentanetetracarboxylate,
$(COOC_2H_5)_2C(C_2H_5)\cdot[CH_2]_3\cdot C(C_2H_5)\cdot(COOC_2H_5)_2$.

The quantities employed in preparing this compound were:—

Ethyl pentanetetracarboxylate......	36·0 grams.
Sodium................	4·6 „
Alcohol	55·0 „
Ethyl iodide	40·0 „

The operation was carried out exactly as described under ethyl dimethylpentanetetracarboxylate (p. 829); as, however, the reaction was not so energetic, the mixture was heated for two hours at 100°. The crude ethereal salt obtained weighed 40 grams, and, on fractionation, distilled, with the exception of very small high and low boiling fractions, between 245° and 250° (30 mm.). The pure substance boils constantly at 247° under a pressure of 30 mm. Analysis gave the following results:—

0·1640 gram substance gave 0·1300 gram H_2O and 0·3650 gram CO_2.

	Theory. $C_{21}H_{36}O_8$.	Found.
C	60·57 per cent.	60·69 per cent.
H	8·65 „	8·80 „
O	30·77 „	30·51 „

Ethyl diethylpentanetetracarboxylate is a thick, colourless oil boiling at 247° (30 mm.).

Diethylpentanetetracarboxylic Acid,
$(COOH)_2C(C_2H_5)\cdot[CH_2]_3\cdot C(C_2H_5)(COOH)_2$.

The hydrolysis of ethyl diethylpentanetetracarboxylate was conducted as described under dimethylpentanetetracarboxylic acid (p. 830). The ethereal solution of the tetrabasic acid was evaporated to a small bulk, allowed to stand, and the crystals which separated collected, washed rapidly with small quantities of pure ether on a filter pump, and dried over sulphuric acid in a vacuum.

The analysis gave the following result:—

0·1553 gram substance gave 0·0957 gram H_2O and 0·2930 gram CO_2.

	Theory. $C_{13}H_{20}O_8$.	Found.
C	51·31 per cent.	51·46 per cent.
H	6·58 „	6·84 „
O	42·11 „	41·70 „

Diethylpentanetetracarboxylic acid is a colourless, crystalline substance which, when heated in a capillary tube, decomposes at about 192—195° with evolution of carbonic anhydride and formation of diethylpimelic acid. It is very readily soluble in water and alcohol, and much more so in ether than the corresponding dimethyl acid, sparingly in benzene:—

The basicity of the acid was determined by titration with standard potassium hydrate solution.

0·1536 gram substance required for neutralisation 0·1118 gram KOH.

A tetrabasic acid of the formula $C_{13}H_{20}O_8$ requires 0·1131 gram KOH.

Silver Diethylpentanetetracarboxylate, $C_{13}H_{16}Ag_4O_8$.—This salt was prepared from the neutral solution of the potassium salt by the addition of silver nitrate solution. The white, insoluble precipitate was collected, washed with water, dried over sulphuric acid in a vacuum, and analysed, with the following result:—

0·2834 gram substance gave on ignition 0·1659 gram silver.

	Theory. $C_{13}H_{16}Ag_4O_8$.	Found.
Ag........	58·90 per cent.	58·54 per cent.

This silver salt is very stable and not readily acted on by light.

Ethyl Diethylpimelate and Diethylpimelic Acid,

$COOH{\cdot}CH(C_2H_5){\cdot}[CH_2]_3{\cdot}CH(C_2H_5){\cdot}COOH$.

Diethylpimelic acid was prepared by heating crude diethylpentanetetracarboxylic acid at 210—220° until the evolution of carbonic anhydride had ceased and then purifying the crude product by conversion into the diethyl salt (see p. 825). Ethyl diethylpimelate is a colourless, agreeably smelling oil which boils constantly at 209—211° (100 mm.).

Analysis:—

0·1317 gram substance gave 0·1222 gram H_2O and 0·3190 gram CO_2.

	Theory. $C_{15}H_{28}O_4$.	Found.
C	66·18 per cent.	66·06 per cent.
H.......	10·29 „	10·31 „
O	23·53 „	23·63 „

The specific gravity of this ethereal salt is *d* 4°/4° = 0·9667; *d* 15°/15° = 0·9583; *d* 25°/25° = 0·9509.

The magnetic rotation determinations gave as an average:—

t.	Sp. rotation.	Mol. rotation.
18·2°	0·9708	15·355

Diethylpimelic acid was prepared from the pure ethereal salt by hydrolysis with alcoholic potassium hydrate (see p. 826). The alkaline solution of the potassium salt, deposits the acid, on acidifying, as a semi-solid mass; this was extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residual solid acid purified by spreading on a porous plate and subsequently recrystallising it from water.

For analysis, the substance was dried over sulphuric acid in a vacuum:—

0·1508 gram substance gave 0·1254 gram H_2O and 0·3362 gram CO_2.

	Theory. $C_{11}H_{20}O_4$.	Found.
C	61·11 per cent.	60·80 per cent.
H	9·26 „	9·24 „
O.......	29·63 „	29·96 „

Diethylpimelic acid crystallises from water in four-sided prisms which resemble crystals of cane sugar in appearance and melt at 96—97°.

Diethylpimelic acid is sparingly soluble in cold water. about 0·234 part in 100 parts of water at 13·5°.

The basicity of this acid was determined by titration with normal potassium hydrate solution:—

0·1710 gram acid required for neutralisation 0·0883 gram KOH.

A bibasic acid of the formula $C_{11}H_{20}O_4$ requires 0·0889 gram KOH.

The dissociation constant for the electrical conductivity of diethylpimelic acid at different concentrations is K = 0·00345

Ethyl Dipropylpentanetetracarboxylate, $(COOC_2H_5)_2C(C_3H_7)\cdot[CH_2]_3\cdot C(C_3H_7)(COOC_2H_5)_2$.

The quantities used in the preparation of this substance were :—

Ethyl pentanetetracarboxylate ...	36·0 grams.
Sodium	4·6 ,,
Alcohol	60·0 ,,
Propyl iodide.................	40·0 ,,

the operation being conducted exactly as described under ethyl dimethylpentanetetracarboxylate. In this instance, however, on mixing the propyl iodide with the alcoholic solution of the disodium salt of ethylic pentanetetracarboxylate, only a slight evolution of heat was observable even after standing for some minutes. The product of the reaction was a thick oil, which, on twice fractioning, boiled constantly at 253—256° (30 mm.) as a colourless oil, which on standing completely solidified.

The crystalline cake was well pressed, dried over sulphuric acid in a vacuum and analysed with the following result :—

0·1583 gram substance gave 0·1290 gram H_2O and 0·3586 gram CO_2.

	Theory. $C_{23}H_{40}O_8$.	Found.
C.......	62·16 per cent.	61·77 per cent.
H	9·00 ,,	9·05 ,,
O.......	28·83 ,,	29·18 ,,

Ethyl dipropylpentanetetracarboxylate melts at about 52—54° and distils at 253—256° (30 mm.); it is very readily soluble in the usual organic solvents.

This ethereal salt gave somewhat curious results on hydrolysis; this was conducted as usual (p. 830), and the resulting syrupy tetrabasic acid, which on standing became completely solid, was freed from traces of oily matter by spreading on a porous plate, and analysed with the following result :—

0·1596 gram substance gave 0·1194 gram H_2O and 0·3278 gram CO_2.

	Theory. $(COOH)_2C(C_3H_7)\cdot[CH_2]_3\cdot C(C_3H_7)(COOH)_2$.	Found.
C	54·21 per cent.	56·01 per cent.
H	7·23 ,,	8·31 ,,
O	38·56 ,,	35·68 ,,

The acid was then dissolved in a small quantity of warm water, filtered, and the solution allowed to stand, when, in a short time, beautiful, four-sided, glistening plates separated; these were collected, washed with a little water, dried on a porous plate over sulphuric acid in a vacuum, and again analysed.

I. 0·1460 gram substance gave 0·1090 gram H_2O and 0·2990 gram CO_2.

II. 0·1433 gram substance gave 0·1075 gram H_2O and 0·2932 gram CO_2.

	Found.		
	I.	II.	
C	55·85	55·80	per cent.
H	8·30	8·34	„

From these analytical results, this beautiful substance appears to be a mixture, in molecular proportion, of dipropylpentanetetracarboxylic acid and dipropylpentanetricarboxylic acid,

$$(COOH)_2C(C_3H_7)\cdot[CH_2]_3\cdot CH(C_3H_7)\cdot COOH;$$

such a mixture contains C = 56·13, H = 7·75 per cent. As, however, the crystals, when critically examined under the microscope, were found to be perfectly homogeneous, it appears probable that these two acids crystallise together in molecular proportion. The composition of these crystals is well borne out by the results obtained by titrating their aqueous solution with standard potassium hydrate solution; the numbers agree again with those required for a mixture of molecular proportions of the tribasic and tetrabasic acids.

0·1640 gram substance required for neutralisation 0·0964 gram KOH.

The mixture of tri- and tetra-basic acids requires 0·1037 gram KOH.

When heated in a capillary tube, these crystals decompose at 168° with evolution of carbonic anhydride and formation of dipropylpimelic acid.

Ethyl Dipropylpimelate and Dipropylpimelic Acid,
$COOH\cdot CH(C_3H_7)\cdot[CH_2]_3\cdot CH(C_3H_7)\cdot COOH$.

The crude acid obtained by the hydrolysis of ethyl dipropylpentanetetracarboxylate was heated in an oil-bath at 200—220°, till all evolution of carbonic anhydride had ceased, and the resulting thick, oily acid converted into the ethyl salt by means of alcohol and sulphuric acid (see p. 825). In this case it was found necessary to fraction the ethereal salt several times before it could be obtained pure.

Ethyl dipropylpimelate boils at 224—226° (100 mm.); it is a moderately thick oil of peculiar odour, closely resembling, though fainter than, that of ethyl pimelate. The analysis gave the following numbers:—

0·1484 gram substance gave 0·1434 gram H_2O and 0·3685 gram CO_2.

	Theory. $C_{17}H_{32}O_4$.	Found.
C	68·00 per cent.	67·73 per cent.
H	10·66 „	10·74 „
O	21·33 „	21·53 „

The specific gravity of ethyl dipropylpimelate is $d\,4°/4° = 0·9578$; $d\,15°/15° = 0·9495$; $d\,25°/25° = 0·9436$.

The magnetic rotation determinations gave—

t.	Sp. rotation.	Mol. rotation.
18°	0·9834	17·296

The hydrolysis of this ethereal salt was carried out exactly as described under ethyl pimelate. The acid, being sparingly soluble in water, separated as a semi-solid mass on acidifying the solution of the alkaline salt; it was extracted with ether as usual, and thus obtained as a thick oil, which on standing became almost solid. The crystalline cake was very carefully pressed, to remove every trace of oily matter, boiled with a large quantity of water, filtered, and the filtrate allowed to cool slowly. After standing for some time, the milky liquid deposited beautiful, four-sided plates; these were collected, dried, first on a porous plate, then at 50°, and analysed, with the following result:—

0·1400 gram substance gave 0·1258 gram H_2O and 0·3290 gram CO_2.

	Theory. $C_{13}H_{24}O_4$.	Found.
C	63·93 per cent.	64·00 per cent.
H	9·84 „	9·98 „
O	26·23 „	26·02 „

Dipropylpimelic acid is sparingly soluble in hot water, and therefore by the above treatment only small quantities can be recrystallised at a time. It appeared interesting to fractionally crystallise the substance by extracting the residual mass from each crystallisation with fresh quantities of boiling water, until, with the exception of a trace of oily impurity, all had been dissolved. In this way five fractions were obtained, melting respectively at 92—94°, 91—93°, 90—92°, 87—90°, 87—89°; all these fractions on crystallisation from light petroleum, melted at 95—96°, which must be taken as the correct melting point of the acid, and this behaviour seems to indicate that the crude acid does not consist of two structural isomers.

Dipropylpimelic acid is very sparingly soluble in cold water. 100 parts of water at 13·5° dissolve only 0·049 part of the pure acid.

The dissociation constant for the electrical conductivity of dipropylpimelic acid at different concentrations is $K = 0·0030$.

Salts of Dipropylpimelic Acid.—The *silver salt*, $C_{13}H_{22}Ag_2O_4$, was prepared by adding silver nitrate to a moderately dilute neutral solution of the potassium salt. It is a white, granular precipitate, apparently insoluble in water. Analysis:—

0·1710 gram substance gave 0·0759 gram H_2O and 0·2142 gram CO_2.

0·3143 gram substance gave, on ignition, 0·1476 gram Ag.

	Theory. $C_{13}H_{22}Ag_2O_4$.	Found.
C	34·13 per cent.	34·33 per cent.
H	4·82 „	4·93 „
Ag.	47·04 „	46·96 „

A dilute neutral solution of the potassium salt shows the following behaviour with reagents:—

Zinc sulphate, a white, caseous precipitate, insoluble in water. *Lead acetate*, a white, apparently crystalline precipitate, somewhat soluble in boiling water. *Copper sulphate*, a light, bluish-green precipitate, insoluble in water. *Barium* and *calcium chlorides*, no precipitate.

Ethyl Diisopropylpentanetetracarboxylate,

$(COOC_2H_5)_2C(C_3H_7)\cdot[CH_2]_3\cdot C(C_3H_7)(COOC_2H_5)_2$.

The method used and the quantities employed in the preparation of this ethereal salt were the same as in the case of the dipropyl compound, isopropyl iodide being substituted for propyl iodide; the yield of crude product was 42·5 grams.

Ethyl diisopropylpentanetetracarboxylate boils at 250—252° (30 mm.). Analysis:—

0·1648 gram substance gave 0·1335 gram H_2O and 0·3730 gram CO_2.

	Theory. $C_{23}H_{40}O_8$.	Found.
C	62·16 per cent.	61·73 per cent.
H	9·00 „	8·99 „
O	28·83 „	29·28 „

This ethereal salt differs from the normal propyl compound in being a thick syrup, which does not solidify when cooled to 0°. On hydrolysis, it yields a solid acid, presumably the corresponding *diisopropylpentanetetracarboxylic acid*; it was not analysed.

Ethyl Diisopropylpimelate and Diisopropylpimelic Acid, $COOH{\cdot}CH(C_3H_7){\cdot}[CH_2]_3{\cdot}CH(C_3H_7){\cdot}COOH$.

In preparing this acid, the acid obtained by the hydrolysis of ethyl diisopropylpentanetetracarboxylate (by the method given on p. 830) was heated at 200° until all effervescence had ceased, and the residual thick, brownish acid converted into the ethyl salt by treatment with alcohol and sulphuric acid. Ethyl diisopropylpimelate, like the normal propyl derivative, must be repeatedly fractioned before it shows a constant boiling point. The specimen used for analysis and for the physical measurements boiled at 220—222° (100 mm.), or only about 4° lower than ethyl dipropylpimelate.

0·1334 gram substance gave 0·1265 gram H_2O and 0·3306 gram CO_2.

	Theory. $C_{17}H_{32}O_4$.	Found.
C	68·00 per cent.	67·58 per cent.
H	10·66 ,,	10·54 ,,
O	21·33 ,,	21·88 ,,

Ethyl diisopropylpimelate is a thick, colourless oil, boiling at 220—222° (100 mm.). Its specific gravity is d 4°/4° = 0·9651; d 15°/15° = 0·9567; d 25°/25° = 0·9507.

The magnetic rotation determinations gave as an average—

t.	Sp. rotation.	Mol. rotation.
19·3°	0·9866	17·238.

The hydrolysis of this ethereal salt, and the isolation and purification of the resulting acid, were conducted exactly as described under ethyl dipropylpimelate (p. 837). The various fractions obtained by recrystallising the crude acid from water melted at the following temperatures:—93—94°, 92—93°, 91—93°.

These, on recrystallisation from light petroleum, melted at 96—98°, and gave the following numbers on analysis:—

0·1440 gram substance gave 0·1290 gram H_2O and 0·3375 gram CO_2.

	Theory. $C_{13}H_{24}O_4$.	Found.
C	63·93 per cent.	63·92 per cent.
H	9·84 ,,	9·95 ,,
O	26·23 ,,	26·13 ,,

Diisopropylpimelic acid melts at 96—98°. It is sparingly soluble in cold water; it is, however, about twice as soluble as the isomeric dipropylpimelic acid, 100 parts of water at 13·5° dissolving about 0·096 part of the pure acid. It crystallises from its solution in hot, light petroleum, on cooling, in beautiful, feathery, needle-shaped crystals.

The dissociation constant for the electrical conductivity of diisopropylpimelic acid at different concentrations is $K = 0{\cdot}0032$.

Ethyl Diisobutylpentanetetracarboxylate,

$(COOC_2H_5)_2C(C_4H_9)\cdot[CH_2]_3\cdot C(C_4H_9)(COOC_2H_5)_2$.

This ethereal salt could, no doubt, be readily obtained by treating the disodium compound of ethyl pentanetetracarboxylate with isobutyl iodide in the usual way, but it appeared to us interesting to determine whether the synthesis of this substance could equally well be performed by treating the sodium compound of ethyl isobutylmalonate with trimethylene bromide, thus:—

$$2(COOC_2H_5)_2CNa\cdot C_4H_9 + BrCH_2\cdot CH_2\cdot CH_2Br = \\ (COOC_2H_5)_2C(C_4H_9)\cdot CH_2\cdot CH_2\cdot CH_2\cdot C(C_4H_9)(COOC_2H_5)_2 + 2NaBr.$$

138 grams of ethyl isobutylmalonate (b. p. 228—233°) was mixed with a cold solution of 15 grams of sodium dissolved in 170 grams of absolute alcohol, 64·5 grams of trimethylene bromide added, and the mixture heated cautiously on a water-bath, in a flask connected with a reflux apparatus. The reaction sets in all at once, the liquid boils vigorously, and quantities of sodium bromide are deposited. After heating for half an hour, the neutral product was mixed with water, extracted three times with ether, the ethereal solution washed well with water, dried over calcium chloride, and evaporated; the almost colourless, oily residue, which weighed about 150 grams, was then subjected to distillation under reduced pressure (200 mm.). As soon as the last traces of ether had distilled over, the thermometer rose rapidly to 200°, between which temperature and 230° about 80 grams passed over; the pressure was then reduced to 60 mm., when the residue distilled almost completely between 250° and 280°, and weighed 58 grams. The higher fraction was subsequently purified by repeated distillation under a pressure of 30 mm., when a considerable quantity of a colourless oil was obtained boiling constantly at 257—263°. The analysis of this gave the following results:—

0·1354 gram substance gave 0·1134 gram H_2O and 0·3135 gram CO_2.

	Theory. $C_{25}H_{44}O_8$.	Found.
C	63·56 per cent.	63·15 per cent.
H	9·33 ,,	9·31 ,,
O	27·11 ,,	27·54 ,,

Ethyl diisobutylpentanetetracarboxylate is a very thick, colourless oil which, on long standing, showed signs of crystallising.

Ethyl Diisobutylpimelate and Diisobutylpimelic Acid,
$COOH{\cdot}CH(C_4H_9){\cdot}[CH_2]_3{\cdot}CH(C_4H_9){\cdot}COOH$.

Ethyl diisobutylpentanetetracarboxylate is very readily hydrolysed by boiling with alcoholic potash, but no attempt was made to purify the resulting tetrabasic acid, the crude substance obtained being at once converted into diisobutylpimelic acid.

52 grams of ethyl diisobutylpentanetetracarboxylate (b. p. 250—275°, 30 mm.) was mixed with a solution of 40 grams of pure potassium hydrate dissolved in 90 per cent. methyl alcohol, the mixture boiled in a reflux apparatus for five hours, and evaporated to dryness; the residue was then dissolved in water and boiled until the last traces of methyl alcohol had been expelled. The alkaline solution thus obtained was acidified with hydrochloric acid, and the oily acid which separated extracted four times with pure ether. The ethereal solution was dried over calcium chloride, evaporated, the crude, tetrabasic acid heated at 200—220° until the evolution of carbonic anhydride had entirely ceased, and the residual impure diisobutylpimelic acid converted into the ethyl salt in the usual way.

Ethyl diisobutylpimelate, under a pressure of 100 mm., boils constantly at 235—237°.

The analysis of this substance gave the following results:—

0·1416 gram substance gave 0·1413 gram H_2O and 0·3598 gram CO_2.

	Theory. $C_{19}H_{36}O_4$.	Found.
C.......	69·51 per cent.	69·30 per cent.
H.......	10·98 ,,	11·09 ,,
O.......	19·51 ,,	19·61 ,,

Ethyl diisobutylpimelate is a colourless oil possessing very similar properties to the other analogously constituted ethereal salts already described.

The specific gravity of this substance is d 4°/4° = 0·9444; d 15°/15° = 0·9363; d 25°/25° = 0·9303.

The magnetic rotation determinations gave as an average—

t.	Sp. rotation.	Mol. rotation.
16·1	0·9952	19·387

The hydrolysis of this ethereal salt was carried out as described under ethyl pimelate. On acidifying the alkaline solution of the potassium salt, the crude diisobutylpimelic acid separates as a thick, gummy mass, and was extracted with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a thick, almost colourless oil which, on standing over sulphuric acid in a vacuum, solidified to a mass of crystals. This crude acid was roughly purified by contact with a porous plate, and then recrystallised from large quantities of boiling water. The analysis gave the following results:—

0·1405 gram substance gave 0·1296 gram H_2O and 0·3399 gram CO_2.

	Theory. $C_{15}H_{28}O_4$.	Found.
C.......	66·17 per cent.	65·98 per cent.
H.......	10·28 „	10·25 „
O.......	23·53 „	23·77 „

Diisobutylpimelic acid melts at about 82—84°, but not very sharply.

It is very sparingly soluble in cold water; 100 parts of water at 13·5° dissolve only about 0·038 part of the pure acid.

The basicity of the acid was determined by titration with standard potassium hydrate solution.

0·1482 gram substance required for neutralisation 0·0605 gram KOH.

A bibasic acid of the formula $C_{13}H_{28}O_4$ requires theoretically 0·0608 gram KOH.

The dissociation constant for the electrical conductivity of diisobutylpimelic acid could not be accurately determined owing to the acid being so sparingly soluble in water.

Ethyl Dibenzylpentanetetracarboxylate,

$(COOC_2H_5)_2C(CH_2{\cdot}C_6H_5){\cdot}[CH_2]_3{\cdot}C(CH_2{\cdot}C_6H_5)(COOC_2H_5)_2$.

This substance was the first derivative of ethyl pentanetetracarboxylate obtained, and its method of preparation differed essentially from that of the derivatives subsequently investigated, and described in the preceding pages. The quantities taken were:—

Ethyl pentanetetracarboxylate................	9 grams.
Sodium, dissolved in 15 grams of alcohol......	1·2 „
Benzyl chloride.........................	9 „

The ethyl pentanetetracarboxylate was dissolved in the cold solution of the sodium ethoxide, the benzyl chloride added, and the mixture heated for two hours in a flask connected with a reflux apparatus.

At the end of this time, the product, which had become quite neutral, was mixed with water, distilled in steam until the excess of benzyl chloride had been completely removed, and the residue extracted with ether. The ethereal solution was dried over anhydrous potassium carbonate, evaporated, and the thick, oily residue allowed to stand over sulphuric acid in a vacuum until it had completely solidified. The crystalline cake was then freed frôm oily matter by spreading it on a porous plate, rapidly washed with small quantities of methyl alcohol on a filter-pump, and the white, granular residue dried over sulphuric acid in a vacuum. The analysis gave the following result:—

0·1588 gram substance gave 0 1063 gram H_2O and 0·3986 gram CO_2.

	Theory. $C_{31}H_{40}O_8$	Found.
C	68·88 per cent.	68·46 per cent.
H......	7·41 ,,	7·43 ,,
O......	23·70 ,,	24·11 ,,

Ethyl dibenzylpentanetetracarboxylate melts at about 75—77°, and when once melted, it often remains for some days as a very thick, semi-solid, transparent mass, which, however, when rubbed with a rod moistened with methyl alcohol, at once solidifies. It is readily soluble in the usual organic solvents.

Dibenzylpentanetetracarboxylic Acid,

$(COOH)_2C(CH_2{\cdot}C_6H_5){\cdot}[CH_2]_3{\cdot}C(CH_2{\cdot}C_6H_5)(COOH)_2$.

In order to obtain this acid, the pure ethereal salt (10 grams) was hydrolysed by boiling with excess of methyl alcoholic potash (10 grams KOH) for two hours in a reflux apparatus. The excess of alcohol was distilled off, the product dissolved in water, evaporated on a water-bath till quite free from alcohol, filtered, and acidified with hydrochloric acid. The thick, gummy mass which separated was extracted four times with ether, the ethereal solution well dried over calcium chloride, evaporated, and the thick, oily residue allowed to stand until it had completely solidified. The solid cake thus obtained was roughly purified by spreading it on a porous plate, the crude, yellowish-white acid ground up in a mortar with pure ether, and subsequently washed on a filter-pump with this solvent until the residual acid was perfectly white. The product consists of pure dibenzylpentanetetracarboxylic acid, as is shown by the following analysis :—

0·1586 gram substance gave 0·0794 gram H_2O and 0·3728 gram CO_2.

	Theory. $C_{23}H_{24}O_8$.	Found.
C.......	64·48 per cent.	64·16 per cent.
H.......	5·61 „	5 55 „
O.......	29·90 „	30 29 „

Dibenzylpentanetetracarboxylic acid decomposes at about 205—207° with evolution of carbonic anhydride and formation of dibenzylpimelic acid :—

$$(COOH)_2(CH_2{\cdot}C_6H_5)C{\cdot}[CH_2]_3{\cdot}C(CH_2{\cdot}C_6H_5)(COOH)_2 = \\ COOH{\cdot}CH(CH_2{\cdot}C_6H_5){\cdot}[CH_2]_3{\cdot}CH(CH_2{\cdot}C_6H_5){\cdot}COOH + 2CO_2.$$

The basicity of the acid was determined by titration with standard potassium hydrate solution.

0·0972 gram acid required for neutralisation 0·0488 gram KOH.

A tetrabasic acid of the formula $C_{23}H_{24}O_8$ requires 0·0509 gram KOH.

Salts of Dibenzylpentanetetracarboxylic Acid.—The *silver salt*, $C_{23}H_{20}Ag_4O_8$, was prepared from a dilute neutral solution of the ammonium salt by the addition of a large excess of silver nitrate solution, the whole being well shaken during the operation. The white, insoluble precipitate thus obtained, after being well washed with water, and dried over sulphuric acid in a vacuum, gave the following results on analysis :—

0·1667 gram substance gave 0·0406 gram H_2O, 0·1938 gram CO_2, and 0·0842 gram Ag.

	Theory. $C_{23}H_{20}Ag_4O_8$.	Found.
C.......	32·32 per cent.	31·70 per cent.
H......	2·34 „	2·70 „
Ag......	50·35 „	50·50 „

A dilute neutral solution of the ammonium salt shows the following behaviour with reagents :—

Copper acetate, a bright-blue precipitate, sparingly soluble in water; on boiling with water, the precipitate becomes almost white. *Calcium chloride*, no precipitate in the cold, but on boiling, the calcium salt separates as a white, crystalline precipitate. *Barium chloride*, no precipitate. *Zinc sulphate* and *lead acetate*, white, amorphous precipitates insoluble in water.

Dibenzylpimelic Acid,

$$COOH{\cdot}CH(CH_2{\cdot}C_6H_5){\cdot}[CH_2]_3{\cdot}CH(CH_2{\cdot}C_6H_5){\cdot}COOH.$$

This acid is produced when dibenzylpentanetetracarboxylic acid is heated at 200—220° until the evolution of carbonic anhydride has completely ceased. The resulting brownish resin can only with difficulty be obtained in a crystalline condition; the purification of this crude product may, however, be readily accomplished in the following way:—The crude acid is dissolved in an excess of a warm, dilute solution of barium hydroxide, heated to boiling, and a current of carbonic anhydride passed until the excess of alkali has been removed. The product is filtered, the precipitated barium carbonate well washed, and the colourless filtrate evaporated until a mass of crystals of the barium salt of the acid separates from the boiling solution; these are rapidly collected, washed with a little boiling water on the filter-pump (the salt is more soluble in cold than hot water), and drained on a porous plate. The mother liquors, on continued evaporation, deposit a further crop of crystals, which are collected in the same manner. The colourless, glistening mass of crystals is dissolved in water, acidified with hydrochloric acid, the precipitated acid extracted with ether, and the ethereal solution dried over calcium chloride and evaporated; as the evaporation proceeds, crystals separate; these are collected, freed from a trace of oily impurity by spreading on a porous plate, and then recrystallised from a mixture of equal parts of benzene and light petroleum. In this way, beautiful, glistening, prismatic crystals are obtained which, as the analyses show, consist of pure dibenzylpimelic acid:—

I. 0·1572 gram substance gave 0·1002 gram H_2O and 0·4265 gram CO_2.

II. 0·1355 gram substance gave 0·0888 gram H_2O and 0·3688 gram CO_2.

III. 0·1384 gram substance gave 0·0894 gram H_2O and 0·3758 gram CO_2.

	Theory. $C_{21}H_{24}O_4$.	Found. I.	II.	III.
C	74·12 p. c.	73·99	74·23	74·05 p. c.
H	7·06 „	7·08	7·28	7·17 „
O	18·82 „	18·93	18·49	18·78 „

Dibenzylpimelic acid melts at 120° with slight previous softening; it is readily soluble in hot benzene, ether, and alcohol, sparingly in light petroleum.

The dissociation constant for the electrical conductivity of dibenzylpimelic acid at different concentrations is $K = 0·0040$.

Salts of Dibenzylpimelic Acid.—The *barium salt*, $C_{21}H_{22}BaO_4 + 3H_2O$(?), is readily prepared by dissolving the pure acid in a solution of barium hydroxide, removing the excess of the latter by passing carbonic anhydride, and evaporating the solution as described above. It is more soluble in cold than in hot water, and separates in pearly plates on boiling its cold concentrated solution.

The analysis of the air-dry salt gave the following results:—

I. 0·5748 gram substance, heated at 100° until constant, lost 0·056 gram H_2O, and the residue, heated with sulphuric acid, gave 0·2554 gram $BaSO_4$.

II. 0·4117 gram substance, heated at 100° till constant, lost 0·0401 gram H_2O.

	Theory.	Found.		
	$C_{21}H_{22}BaO_4 + 3H_2O$.	I.	II.	
Ba	25·90 per cent.	26·10	—	per cent.
H_2O	10·21 „	9·70	9·74	„

This salt appears to lose some of its water of crystallisation on long standing in the air.

A moderately dilute neutral solution of the potassium salt shows the following behaviour with reagents:—

Barium chloride, on boiling, a white precipitate, sparingly soluble in hot water, but more soluble in cold water. *Calcium chloride*, no precipitate in the cold, but, on boiling, a white calcium salt separates which redissolves on cooling. *Zinc acetate*, a white, caseous precipitate, sparingly soluble in water. *Copper acetate*, a beautiful light-blue precipitate, insoluble in water. *Lead acetate*, a white, amorphous, very sparingly soluble precipitate.

Attempt to Prepare Monobenzylpimelic Acid,

$COOH·CH(CH_2·C_6H_5)·[CH_2]_3·CH_2·COOH$.

In the preceding pages the preparation of some disubstituted derivatives of pimelic acid from the disodium compound of ethyl pentanetetracarboxylate has been described, and it appeared to us of interest to determine whether by employing the monosodium compound of this ethereal salt, monosubstituted derivatives such as monomethyl- and monobenzyl-pimelic acids would also be obtained. The example selected was the preparation of monobenzylpimelic acid, as it was thought probable that the reaction could be more readily followed in this case than in the case of the lower homologues.

9 grams of ethyl pentanetetracarboxylate (1 mol.) was mixed with a solution of 0·6 gram of sodium (1 mol.) in absolute alcohol, 4 grams of benzyl chloride (1 mol.) added, and the mixture heated in a reflux apparatus for two hours. The product was then diluted with water, extracted with ether, and the ethereal solution washed well, dried over calcium chloride, and evaporated. In this way, 11 grams of a yellowish oil was obtained, which, even on long standing over sulphuric acid in a vacuum, did not crystallise, although a distinct scum formed on the surface.

The ethereal salt was hydrolysed by boiling with a methyl alcoholic solution of 11 grams of potassium hydrate for two hours, the alcohol removed by evaporation with the addition of water, and the cold alkaline solution acidified with dilute hydrochloric acid. The thick, resinous mass which separated was extracted ten times with ether, the ethereal solution dried over calcium chloride, evaporated, and the transparent, resinous mass, which, even after standing for some days over sulphuric acid in a vacuum, showed no signs of crystallising, was stirred well with warm water of 40°. In a short time the mass began to get hard and opaque, and on constantly changing the water a solid mass was ultimately obtained. This was dried on a porous plate at the ordinary temperature, ground up in a mortar with pure ether, and the insoluble tetracarboxylic acid which separates washed on a filter pump with small quantities of ether until it had become perfectly colourless.

The analysis of the substance, dried over sulphuric acid in a vacuum, gave:—

0·1376 gram substance gave 0·0744 gram H_2O and 0·3239 gram H_2O.

	Theory.		
	Monobenzylpentanetetracarboxylic acid = $C_{16}H_{18}O_8$.	Dibenzylpentanetetracarboxylic acid = $C_{23}H_{24}O_8$.	Found.
C........	56·80 p. c.	64·48 p. c.	64·20 p. c.
H........	5·33 ,,	5·61 ,,	6·01 ,,
O........	37·87 ,,	29·90 ,,	29·79 ,,

Dibenzylpentanetetracarboxylic acid had therefore been formed in this reaction instead of the monobenzyl derivative. This interesting point was confirmed by an investigation of the properties of the acid, and an analysis of the silver salt:—

0·2120 gram of the dry silver salt gave on ignition 0·1063 gram Ag.

	Theory. $C_{23}H_{20}Ag_4O_8$.	Found.
Ag......	50·35 per cent.	50·14 per cent.

In order, if possible, to further follow the course of this reaction, the aqueous extract of the crude dibenzylpentanetetracarboxylic acid (see above) was carefully examined. The combined extracts were neutralised with sodium hydrate, evaporated to a small bulk, acidified, extracted with pure ether, the ethereal solution dried over calcium chloride and evaporated, and the residual, thick, yellow oil allowed to stand for some days over sulphuric acid in a vacuum. As the oil showed no signs of crystallising, it was transferred to a flask, and heated in an oil-bath at 220° until the evolution of carbonic anhydride had ceased. The residual, dark-coloured acid was then dissolved in dilute sodium hydrate solution, boiled for two hours with freshly-ignited animal charcoal, and filtered. The almost colourless alkaline solution was evaporated to a small bulk, acidified, extracted five times with ether, the ethereal solution dried over calcium chloride, evaporated, and the oily residue set aside until it had completely solidified. The crude product, which showed the properties of pimelic acid, was roughly purified by spreading it on a porous plate, then converted into the calcium salt, and this salt, after recrystallisation, decomposed with hydrochloric acid, and the resulting acid finally recrystallised from benzene.

The white, crystalline powder thus obtained melted at 100—102° and consisted of pure pimelic acid, as is shown by the following analysis:—

0·1322 gram substance gave 0·0908 gram H_2O and 0·2542 gram CO_2.

	Theory. $COOH\cdot[CH_2]_5\cdot COOH$.	Found.
C	52·50 per cent.	52·44 per cent.
H	7·50 ,,	7·63 ,,
O	40·00 ,,	39·93 ,,

This experiment proves that, under the conditions employed, ethyl monobenzylpentanetetracarboxylate is not formed, the reaction, on the contrary, giving rise to the production of ethyl dibenzylpentanetetracarboxylate; one half of the ethyl pentanetetracarboxylate either takes no part whatever in the decomposition or is regenerated from the monosodium compound, as shown in the introduction.

Action of Benzal Chloride on the Disodium Compound of Ethyl Pentanetetracarboxylate. Formation of Dibenzalpimelic Acid,

$COOH{\cdot}C({:}CH{\cdot}C_6H_5){\cdot}[CH_2]_3{\cdot}C({:}CH{\cdot}C_6H_5){\cdot}COOH$.

This remarkable reaction was first instituted with the object of preparing phenylhexamethylene derivatives, as explained in the introduction. 9 grams of ethyl pentanetetracarboxylate was dissolved in a solution of 1·2 grams of sodium in 30 grams of absolute alcohol, 4·2 grams of benzal chloride added, and the mixture heated for five hours in a flask connected with a reflux apparatus. The product was then mixed with water, extracted with ether, the ethereal solution washed with water, and evaporated, and the residual thick, yellowish oil hydrolysed by boiling it with twice the calculated quantity of methyl alcoholic potash for three hours. The alcohol was removed by mixing the product with water and boiling vigorously, the cold alkaline solution acidified with hydrochloric acid, and the resinous precipitate extracted with ether. The ethereal solution was then evaporated, and the yellow, oily residue stirred for two days with fresh quantities of water, until it had become quite solid.

The very crude acid thus obtained was collected, washed with water, allowed to dry on a porous plate, and then heated at 200—220°, until the evolution of carbonic anhydride had ceased. The dark-brown residue was dissolved in dilute sodium hydrate, and the solution boiled with freshly-ignited animal charcoal, by which means a quantity of impurity was removed; the acid was then reprecipitated with hydrochloric acid, washed well, and allowed to dry on a porous plate. The thoroughly dry, dark-yellow substance was ground up in a mortar, exhausted three times with boiling benzene, the residue dissolved in methyl alcohol, and the solution allowed to evaporate nearly to dryness at the ordinary temperature.

The crystals which were deposited were collected, washed with methyl alcohol, recrystallised twice from this solvent, and the magnificent, glistening prisms thus obtained analysed, with the following result:—

I. 0·1192 gram substance gave 0·0672 gram H_2O and 0·3270 gram CO_2.

II. 0·1521 gram substance gave 0·0834 gram H_2O and 0·4183 gram CO_2.

	Theory. $C_{21}H_{20}O_4$.	Found. I.	Found. II.
C	75·00 per cent.	74·81	75·00 per cent.
H	5·95 ,,	6·26	6·09 ,,
O	19·05 ,,	18·93	18·91 ,,

Dibenzalpimelic acid melts at 192—193°. It is readily soluble in hot ethyl and methyl alcohol, sparingly in chloroform and carbon bisulphide, and only very sparingly in benzene, toluene, light petroleum, and water. When strongly heated in small quantities in a test-tube, the acid distils with apparently very little decomposition, and the slightly yellowish distillate solidifies completely on rubbing with a glass rod. Dibenzalpimelic acid, being an unsaturated acid, is instantly oxidised by potassium permanganate in alkaline solution, and at the same time a very strong odour of benzaldehyde is noticeable.

The basicity of the acid was determined first by titration with a standard solution of potassium hydrate:—

0·1264 gram of the pure acid required for neutralisation 0·0425 gram KOH.

This amount of a bibasic acid of the formula $C_{21}H_{20}O_4$ requires 0·0421 gram KOH.

Salts of Dibenzalpimelic Acid.—The *silver salt*, $C_{21}H_{18}O_4Ag_2$, was prepared by adding silver nitrate to a neutral solution of the potassium salt. The white, amorphous precipitate thus produced was collected, washed with water, dried over sulphuric acid on a porous plate, and analysed, with the following result:—

0·1990 gram substance gave 0·0586 gram H_2O and 0·3314 gram CO_2.

0·3308 gram substance gave on ignition 0·1232 gram Ag.

	Theory. $C_{21}H_{18}O_4Ag_2$.	Found.
C	45·90 per cent.	45·42 per cent.
H	3·28 „	3·27 „
Ag......	39·16 „	39·63 „

The neutral solution of the potassium salt gives, with solutions of *barium chloride*, *calcium chloride*, *zinc sulphate*, and *lead acetate*, white, amorphous precipitates, almost insoluble in water. *Copper sulphate* gives a fine, pale-blue, amorphous precipitate, almost insoluble in water.

In order, if possible, to obtain some further clue to the formation of dibenzalpimelic acid in the above decomposition, the aqueous liquors from the hydrolysis of the crude product of the reaction, from which the crude dibenzalpimelic acid had been precipitated by hydrochloric acid, as described above, were extracted five times with ether, the ethereal extract carefully dried over calcium chloride and evaporated. A small quantity of an oily acid was thus obtained, which, after purification by conversion into the calcium salt and recrystallisation from benzene, melted at 100—102°. and showed all the properties of pimelic acid. There could be no doubt as to its identity, although the quantity was too small for analysis.

It appears, therefore, that in this decomposition some ethyl pentanetetracarboxylate is regenerated, which, on hydrolysis and subsequent heating at 200°, is converted into pimelic acid.

For convenience of reference we append, in tabular form, the principal properties of the substances described in this paper.

Pentanetetracarboxylic Acid and its Derivatives.

	Decomposing point.	Boiling point of ethyl salt (30 mm.).
Pentanetetracarboxylic acid	Above 120°	230—235°
Dimethylpentanetetracarboxylic acid	200—205°	238—240°
Diethylpentanetetracarboxylic acid	192—195°	247°
Dipropylpentanetetracarboxylic acid	—	253—256° (M. p. = 52—54°)
Diisopropylpentanetetracarboxylic acid	—	250—252°
Diisobutylpentanetetracarboxylic acid	—	257—263°
Dibenzylpentanetetracarboxylic acid	205—207°	(M. p. = 75—77°)
Dibromopentanetetracarboxylic acid	—	(M. p. = 45°).

Pimelic Acid and its Derivatives.

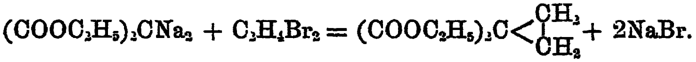
	Acid.			Ethyl salt.		
	Melting point.	Solubility in 100 pts. of water at 13·5°.	Dissociation constants = K.	Boiling point (100 mm.).	Sp. gr. at 15°/15°.	Magnetic rotation.
Pimelic acid	100—102	2·52	0·00311	192—194°	0·9988	11·421
Dimethylpimelic acid	74—76	2·19	0·00337	195—196	0·9728	13·298
Diethylpimelic acid	96—97	0·234	0·00345	209—210	0·9583	15·355
Dipropylpimelic acid	95—96	0·049	0·0030	224—226	0·9495	17·296
Diisopropylpimelic acid	96—98	0·096	0·0032	220—222	0·9567	17·238
Diisobutylpimelic acid	82—84	0·038	—	235—237	0·9363	19·387
Dibenzylpimelic acid	120	—	0·0040	—	—	—
Dibenzalpimelic acid	192—193	—	—	—	—	—

LXXVIII.—*The Synthetical Formation of Closed Carbon Chains.* Part I (continued). *The Action of Ethylene Bromide on the Sodium Compounds of Ethyl Acetoacetate and Ethyl Benzoylacetate.*

By T. Rhymer Marshall, D.Sc., and W. H. Perkin, Jun., Ph.D., F.R.S.

In the study of the synthetical formation of closed carbon chains, one of the most difficult problems has been the determination of the constitution of those substances which are produced when ethylene bromide reacts with the sodium compounds of ethyl malonate, ethyl acetoacetate, and ethyl benzoylacetate.

Taking in the first place the product of the action of ethylene bromide on the sodium compound of ethyl malonate, this substance may be represented either as ethyl trimethylenedicarboxylate (Perkin, Trans., 1885, **47**, 807; 1887, **51**, 849; *Ber.*, **17**, 54), or as ethyl vinylmalonate (Fittig, Roeder, *Ber.*, **16**, 372):

I. 

$$(COOC_2H_5)_2CNa_2 + C_2H_4Br_2 = (COOC_2H_5)_2C{<}\begin{matrix}CH_2\\ | \\ CH_2\end{matrix} + 2NaBr.$$

II. $(COOC_2H_5)_2CNa_2 + C_2H_4Br_2 = (COOC_2H_5)_2CH{\cdot}CH{:}CH_2 + 2NaBr.$

The difficulty in distinguishing between these formulæ lies in the fact that the acid obtained from this ethereal salt by hydrolysis behaves in some respects as an unsaturated acid, whereas in other respects its reactions point to its being a saturated substance. The careful study of the chemical properties and the magnetic rotation of the ethereal salt has, however, left scarcely any doubt that this substance is, in reality, ethyl trimethylenedicarboxylate, and this view of its constitution has received additional support from the very interesting work of Buchner on trimethylene derivatives (*Synthesen von Pyrazol-, Pyrazolin- und Trimethylen-derivaten mittels Diazoessigäther: Habilitationsschrift*, München, 1891).

Baeyer's permanganate test, which of late has come so much into prominence, has been applied by Buchner as a means of discriminating between trimethylene derivatives and unsaturated substances.

This test is based on the fact, first observed by Baeyer (*Annalen*, **245**, 146), that dilute alkaline solutions of unsaturated acids decolorise potassium permanganate instantly, whereas in the case of saturated acids, the pink colour often remains unchanged for days.

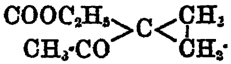
Büchner thus found that trimethylenedicarboxylic acid, and in fact all the trimethylenecarboxylic acids as yet described, behave as saturated substances, and therefore cannot be vinyl derivatives.

Turning now to the product of the action of ethylene bromide on the sodium derivative of ethyl acetoacetate, the problem of assigning the correct constitution to this substance is found to be much more difficult.

The reaction in question undoubtedly proceeds as follows:—

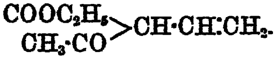
$$2CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + C_2H_4Br_2 = C_8H_{12}O_3 + CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + 2NaBr.$$

There are four formulæ which may be devised to represent the constitution of this ethereal salt $C_8H_{12}O_3$, namely:—

I. 

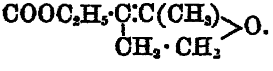
$$\begin{matrix}COOC_2H_5\\CH_3{\cdot}CO\end{matrix}>C<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$$

Ethyl acetyltrimethylenecarboxylate.

II. 

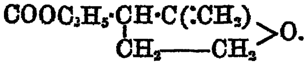
$$\begin{matrix}COOC_2H_5\\CH_3{\cdot}CO\end{matrix}>CH{\cdot}CH{:}CH_2.$$

Ethyl vinylacetoacetate.

III. 

$$\begin{matrix}COOC_2H_5{\cdot}C{:}C(CH_3)\\|\qquad\qquad\\CH_2{\cdot}CH_2\quad\end{matrix}>O.$$

Ethyl methyldehydropentonecarboxylate.

IV. 

$$\begin{matrix}COOC_2H_5{\cdot}CH{\cdot}C({:}CH_2)\\|\qquad\qquad\\CH_2{-\!\!-\!\!-}CH_2\quad\end{matrix}>O.$$

Ethyl methylenetetrahydrofurfurancarboxylate.

The formation of the compounds represented in I and II corresponds with the formation of ethyl trimethylenedicarboxylate and ethyl vinylmalonate respectively, as represented by the equations at the commencement of this paper.

Ethyl methyldehydropentonecarboxylate (III) would be produced as follows:—

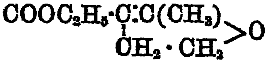
$$CH_3{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + C_2H_4Br_2 = CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CH_2Br){\cdot}COOC_2H_5 + NaBr.$$

Ethyl ω-bromethylacetoacetate.

This intermediate product, under the influence of a second molecule of ethyl sodacetoacetate, loses 1 mol. of hydrogen bromide, thus:—

$$CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CH_2Br){\cdot}COOC_2H_5 = CH_3{\cdot}C(OH){:}C(CH_2{\cdot}CH_2Br){\cdot}COOC_2H_5 =$$

Labile form.



$$\begin{matrix}COOC_2H_5{\cdot}C{:}C(CH_3)\\|\qquad\qquad\\CH_2{\cdot}CH_2\quad\end{matrix}>O + HBr,$$

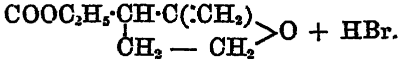
a reaction which is similar to that which has been proved to take place between ethyl sodacetoacetate and trimethylene bromide (Trans., 1887, **51**, 702—727; Lipp, *Ber.*, **18**, 3277).

Ethyl methylenetetrahydrofurfurancarboxylate (IV) may be supposed to be produced from ethyl *ω*-bromethylacetoacetate in the following way:—

$$CH_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CH_2Br){\cdot}COOC_2H_5 =$$

$$CH_2{:}C(OH){\cdot}CH(CH_2{\cdot}CH_2Br){\cdot}COOC_2H_5 =$$

Labile form.



$$\begin{array}{l} COOC_2H_5{\cdot}CH{\cdot}C({:}CH_2) \\ \qquad\quad\;\; | \\ \qquad\quad CH_2 - CH_2 \end{array}\!\!>O + HBr.$$

In previous investigations (Perkin, Trans., 1885, **47**, 801; Freer and Perkin, Trans., 1887, **51**, 820), experiments on the behaviour of the ethereal salt $C_8H_{12}O_3$, and the corresponding acid $C_6H_8O_3$, under the influence of various reagents, were described, and the results thus obtained were shown to lead to the conclusion that this ethereal salt consisted for the most part of ethyl acetyltrimethylenecarboxylate mixed with varying, but usually very small, quantities of ethyl methyldehydropentonecarboxylate.

Subsequently Lipp (*Ber.*, **22**, 1210; compare Colman and Perkin, Trans., 1889, **55**, 358) repeated these experiments, and came to the conclusion that this ethereal salt was ethyl methylenetetrahydrofurfurancarboxylate,* and could not possibly be ethyl acetyltrimethylenecarboxylate.

Owing to these conflicting opinions, it appeared to us that it would be interesting to still further investigate the subject, and in doing so we have obtained a number of results, which, as we believe, conclusively prove that this ethereal salt $C_8H_{12}O_3$ is (as was already suggested by Freer and Perkin) a mixture of ethyl acetyltrimethylenecarboxylate and ethyl methyldehydropentonecarboxylate, the former as a rule largely predominating.

In discussing the question of the constitution of these substances, it will perhaps be best to take each of the possible formulæ separately, and then, by submitting it to the test of experimental evidence, to endeavour to discriminate between them.

As already stated, the ethereal salt $C_8H_{12}O_3$ undoubtedly contains traces of a second substance, but, for the sake of simplicity, the pre-

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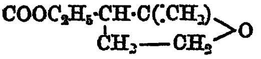
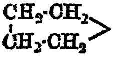
* Lipp names the substance



$$\begin{array}{l} COOC_2H_5{\cdot}CH{\cdot}C({:}CH_2) \\ \qquad\quad\;\; | \\ \qquad\quad CH_2 - CH_2 \end{array}\!\!>O$$

"ethyl trihydromethylenefurfurancarboxylate;" but an examination of the formula reveals at once the fact that this substance is a derivative of tetrahydrofurfuran,



$$\begin{array}{l} CH_2{\cdot}CH_2 \\ | \\ CH_2{\cdot}CH_2 \end{array}\!\!>O,$$

i.e., ethyl methylenetetrahydrofurfurancarboxylate.

sence of this substance may in the meantime be left out of consideration without in the least affecting the question of the constitution of the ethereal salt itself.

Firstly, then, this ethereal salt $C_8H_{12}O_3$ cannot be *ethyl vinylacetoacetate*, $CH_3·CO·CH(CH{:}CH_2)·COOC_2H_5$, because—

1. On hydrolysis, it yields the corresponding acid, $C_6H_8O_3$, without decomposition (Trans., 1885, **47**, 831). Ethyl vinylacetoacetate would, under similar conditions, act presumably like all other monosubstituted derivatives of ethyl acetoacetate, and be completely decomposed into vinylacetone and acetic and vinylacetic acids :—

$$2CH_3·CO·CH(CH{:}CH_2)·COOC_2H_5 + 4KOH = CH_3·CO·CH_2·CH{:}CH_2 \\ + CH_2{:}CH·CH_2·COOK + CH_3·COOK + K_2CO_3 + 2C_2H_5·OH.$$

(Compare hydrolysis of ethyl allylacetoacetate.)

2. Ethyl vinylacetoacetate, being a monosubstituted derivative of ethyl acetoacetate, should, when treated with sodium ethylate and an alkyl iodide such as isoamyl iodide, yield a higher homologue, *e.g.*, ethyl isoamylvinylacetoacetate, thus :—

$$CH_3·CO·CNa(CH{:}CH_2)·COOC_2H_5 + C_5H_{11}I = \\ CH_3·CO·C(C_5H_{11})(CH{:}CH_2)·COOC_2H_5 + NaI.$$

Similarly, ethyl ethylacetoacetate, when treated with sodium ethylate and ethylene bromide, should yield ethyl ethylvinylacetoacetate, which should possess properties similar to those of the ethereal salt $C_8H_{12}O$:—

$$2CH_3·CO·CNa(C_2H_5)·COOC_2H_5 + C_2H_4Br_2 = \\ CH_3·CO·C(C_2H_5)(CH{:}CH_2)·COOC_2H_5 + CH_3·CO·CH(C_2H_5)·COOC_2H_5 \\ + 2NaBr.$$

Neither of these reactions was found to take place on instituting the experiments.

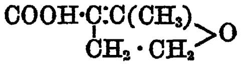
3. Baeyer's permanganate test shows the acid $C_6H_8O_3$ to be a saturated acid, whereas vinylacetoacetic acid is unsaturated.

4. The magnetic rotation of the pure ethereal salt $C_8H_{12}O_3$ is 8·198, whereas the magnetic rotation of ethyl vinylacetoacetate (calculated from that of ethyl allylacetoacetate) would be 9·360 (Trans., 1887, **51**, 822, 823, 828).

Secondly. The substance $C_8H_{12}O_3$ cannot be the ethereal salt of methyldehydropentonecarboxylic acid, because this acid has been prepared by us, and differs very widely from the acid $C_6H_8O_3$ obtained by the hydrolysis of the ethereal salt $C_8H_{12}O_3$, as is seen from the following table :—

Acid $C_6H_8O_3$.	*Methyldehydropentonecarboxylic Acid.*
Oil.	White crystals, m. p. 150°.
Miscible with water.	Only moderately soluble in water.
Gives with hydroxylamine an oxime, $C_6H_9NO_3$.	Is not acted on by hydroxylamine.
On distillation yields acetyltrimethylene, b. p. 112°, which is not acted on by water.	On distillation yields methyldehydropentone, b. p. 82°, which, in contact with water is converted into acetopropyl alcohol.
Is not oxidised by potassium permanganate in dilute alkaline solution.	The dilute alkaline solution of this acid reduces potassium permanganate instantly.

That the acid described above as methyldehydropentonecarboxylic acid has the constitution represented by the formula



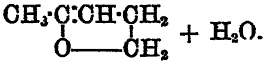
$$\begin{array}{l}\mathrm{COOH\cdot C{:}C(CH_3)} \\ \qquad | \\ \qquad \mathrm{CH_2\cdot CH_2}\end{array} > \mathrm{O}$$

is rendered extremely probable by the following considerations:—

This acid, on distillation, yields methyldehydropentone and carbon dioxide. Methyldehydropentone dissolves in water, and is converted into acetopropyl alcohol; it is therefore the anhydride of acetopropyl alcohol, and the acid must be the carboxylic acid of the anhydride of acetopropyl alcohol.

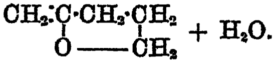
In forming an internal anhydride, acetopropyl alcohol can lose the elements of water in two ways:—

$$\mathrm{I.\ CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH = \underset{Labile\ form.}{CH_3\cdot C(OH){:}CH\cdot CH_2\cdot CH_2\cdot OH} =}$$



$$\begin{array}{l}\mathrm{CH_3\cdot C{:}CH\cdot CH_2} \\ \quad | \qquad\quad | \\ \quad \mathrm{O}\text{———}\mathrm{CH_2}\end{array} + \mathrm{H_2O}.$$

$$\mathrm{II.\ CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH = \underset{Labile\ form.}{CH_2{:}C(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH} =}$$



$$\begin{array}{l}\mathrm{CH_2{:}C\cdot CH_2\cdot CH_2} \\ \quad | \qquad\quad | \\ \quad \mathrm{O}\text{———}\mathrm{CH_2}\end{array} + \mathrm{H_2O}.$$

Apart from the improbable nature of the process, which, as far as we know, is without analogy, the reaction II, involving the participation of the methyl group in the anhydride formation, is unlikely for several reasons, especially as a similar internal anhydride is formed from benzoylpropyl alcohol, $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$ (Trans., 1887, **57**, 838).

In this communication we shall therefore assume that the formula given above to methyldehydropentonecarboxylic acid is correct.

Thirdly. The substance $C_8H_{12}O_3$ cannot be the ethereal salt of methylenetetrahydrofurfurancarboxylic acid, because :—

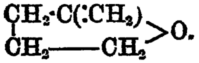
1. All furfurancarboxylic acids hitherto investigated in cold dilute alkaline solution instantly decolorise potassium permanganate solution (Baeyer, *Annalen*, **256**, 193), whereas the acid $C_6H_8O_3$ is not oxidised by permanganate under these conditions.

2. The acid $C_6H_8O_3$ is a ketonic acid, because when treated with hydroxylamine it yields an oxime, $C_6H_9NO_3$.

3. The acid $C_6H_8O_3$, on reduction, takes up in the first place 2 atoms of hydrogen, yielding an acid of the formula $C_6H_{10}O_3$, which, on further reduction, is converted into α-ethyl-β-hydroxybutyric acid, $CH_3\cdot CH(OH)\cdot CH(C_2H_5)\cdot COOH$.

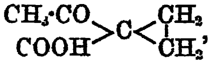
This reaction, it appears to us, cannot be explained in any simple manner on the assumption that the acid $C_6H_8O_3$ is methylenetetrahydrofurfurancarboxylic acid.

Similarly, the substance C_5H_8O, which is produced from the acid $C_6H_8O_3$ by the elimination of carbon dioxide, is a ketone yielding an oxime, C_5H_9NO; this ketone, on reduction, is converted into methylpropylcarbinol. These two facts show that it cannot be methylenedihydrofurfuran,



$$\left.\begin{array}{l}CH_2\cdot C(:CH_2)\\ |\\ CH_2\text{——}CH_2\end{array}\right>O.$$

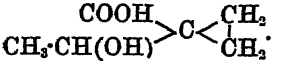
Fourthly. The following considerations prove, as it appears to us, that the acid $C_6H_8O_3$ is acetyltrimethylenecarboxylic acid,



$$\left.\begin{array}{r}CH_3\cdot CO\\ COOH\end{array}\right>C<\begin{array}{l}CH_2\\ |\\ CH_2\end{array},$$

and that the original ethereal salt $C_8H_{12}O_3$ is therefore ethyl acetyltrimethylenecarboxylate.

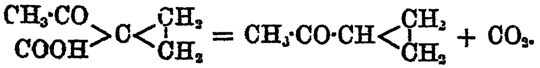
1. It is a monobasic ketonic acid, and as such yields an oxime, $C_6H_9NO_3$. On reduction it is converted into hydroxyethyltrimethylenecarboxylic acid,



$$\left.\begin{array}{r}COOH\\ CH_3\cdot CH(OH)\end{array}\right>C<\begin{array}{l}CH_2\\ |\\ CH_2\end{array}.$$

2. It is a saturated acid, as is shown by Baeyer's permanganate test.

3. On distillation, it is converted into acetyltrimethylene with elimination of carbon dioxide :



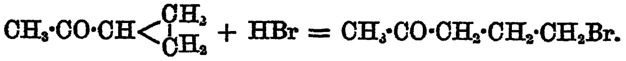
$$\left.\begin{array}{r}CH_3\cdot CO\\ COOH\end{array}\right>C<\begin{array}{l}CH_2\\ |\\ CH_2\end{array} = CH_3\cdot CO\cdot CH<\begin{array}{l}CH_2\\ |\\ CH_2\end{array} + CO_2.$$

Acetyltrimethylene is a ketone; it dissolves readily in sodium hydrogen sulphite solution, and when treated with hydroxylamine yields a beautifully crystalline oxime, C_5H_9NO.

4. It is also interesting to note that the above-mentioned substances

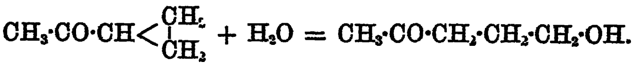
show some remarkable reactions which are analogous to those first noticed in the case of trimethylene and trimethylenedicarboxylic acid.

Thus acetyltrimethylene, in contact with fuming hydrobromic acid, is converted quantitatively into acetopropyl bromide:



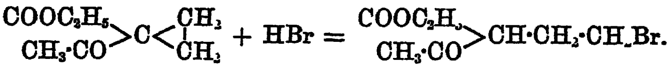
$$\mathrm{CH_3\cdot CO\cdot CH}<\begin{matrix}\mathrm{CH_2}\\|\\\mathrm{CH_2}\end{matrix} + \mathrm{HBr} = \mathrm{CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2Br}.$$

When heated with dilute hydrochloric acid at 100°, acetyltrimethylene is hydrolysed with formation of acetopropyl alcohol:



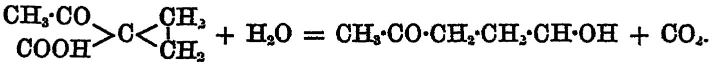
$$\mathrm{CH_3\cdot CO\cdot CH}<\begin{matrix}\mathrm{CH_2}\\|\\\mathrm{CH_2}\end{matrix} + \mathrm{H_2O} = \mathrm{CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH}.$$

Ethyl acetyltrimethylenecarboxylate dissolves readily in fuming hydrobromic acid with formation of ethyl ω-bromethylacetoacetate:



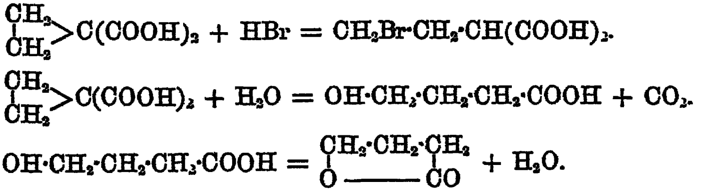
$$\begin{matrix}\mathrm{COOC_2H_5}\\\mathrm{CH_3\cdot CO}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2}\\|\\\mathrm{CH_2}\end{matrix} + \mathrm{HBr} = \begin{matrix}\mathrm{COOC_2H_5}\\\mathrm{CH_3\cdot CO}\end{matrix}>\mathrm{CH\cdot CH_2\cdot CH_2Br}.$$

Acetyltrimethylenecarboxylic acid, on prolonged boiling with water, is converted into acetopropyl alcohol, with elimination of carbon dioxide:



$$\begin{matrix}\mathrm{CH_3\cdot CO}\\\mathrm{COOH}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH_2}\\|\\\mathrm{CH_2}\end{matrix} + \mathrm{H_2O} = \mathrm{CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH\cdot OH} + \mathrm{CO_2}.$$

Reactions similar to the above have been noticed in the case of trimethylenedicarboxylic acid. Fittig and Roeder (*Ber.*, 16, 2592) have shown that this acid in contact with hydrobromic acid yields ω-bromethylmalonic acid, and that when digested with dilute sulphuric acid, it is converted into butyrolactone with evolution of carbon dioxide:—

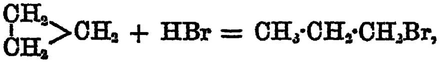


$$\begin{matrix}\mathrm{CH_2}\\|\\\mathrm{CH_2}\end{matrix}>\mathrm{C(COOH)_2} + \mathrm{HBr} = \mathrm{CH_2Br\cdot CH_2\cdot CH(COOH)_2}.$$

$$\begin{matrix}\mathrm{CH_2}\\|\\\mathrm{CH_2}\end{matrix}>\mathrm{C(COOH)_2} + \mathrm{H_2O} = \mathrm{OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH} + \mathrm{CO_2}.$$

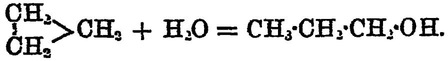
$$\mathrm{OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH} = \begin{array}{l}\mathrm{CH_2\cdot CH_2\cdot CH_2}\\|\qquad\qquad\;\;|\\\mathrm{O}\text{———}\mathrm{CO}\end{array} + \mathrm{H_2O}.$$

Again, trimethylene itself is readily acted on by hydrobromic acid, yielding propyl bromide:



$$\begin{matrix}\mathrm{CH_2}\\|\\\mathrm{CH_2}\end{matrix}>\mathrm{CH_2} + \mathrm{HBr} = \mathrm{CH_3\cdot CH_2\cdot CH_2Br},$$

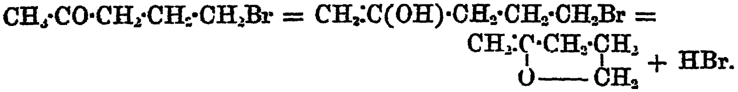
and Gustavson (*J. pr. Chem.* [2], **36**, 300) has lately made the interesting observation that trimethylene in contact with sulphuric acid is converted into propyl alcohol:



$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>CH_2 + H_2O = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}OH.$$

It will thus be seen that acetyltrimethylenecarboxylic acid and acetyltrimethylene show the reactions of trimethylene derivatives.

Lipp (*Ber.*, **22**, 1210) objects to these substances being represented as trimethylene derivatives, principally on the ground that acetopropyl bromide, when treated with solid potassium hydrate, yields a substance boiling at 110—111° which is isomeric with methyldehydropentone, and which he suggests is identical with our acetyltrimethylene. This decomposition he formulates thus:—

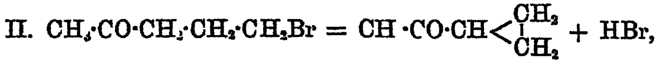


$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br = CH_2{:}C(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br = \begin{matrix}CH_2{:}C{\cdot}CH_2{\cdot}CH_2\\ |\qquad\quad |\\ O \text{———} CH_2\end{matrix} + HBr.$$

This substance (methylenetetrahydrofurfuran) combines with phenylhydrazine, and Lipp therefore at once concludes that this property can no longer be accepted as final in distinguishing ketones from furfuran derivatives, and that, moreover, the experiment proves that the whole series of substances described by us as trimethylene derivatives are in reality tetrahydrofurfuran derivatives.

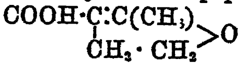
But Lipp has overlooked the fact that the decomposition of acetopropyl bromide by potassium hydrate may also be represented by either of the following equations:—

$$\text{I. } CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH{:}CH_2 + HBr,$$

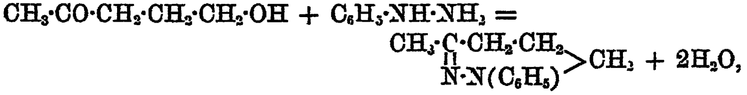


$$\text{II. } CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br = CH\ {\cdot}CO{\cdot}CH\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + HBr,$$

and, as a result of our experiments, there can be no doubt that Lipp's substance is, in reality, acetyltrimethylene, and this being a ketone naturally combines with phenylhydrazine.

Moreover, it is shown in the body of this paper that methyldehydropentonecarboxylic acid,  $\begin{matrix}COOH{\cdot}C{:}C(CH_3)\\ |\qquad\qquad\\ CH_2 \cdot CH_2\end{matrix}\!\!>O$, although its constitution is similar to that of Lipp's hypothetical methylenetetrahydrofurfuran, does not combine with hydroxylamine or phenylhydrazine at the ordinary temperature; and thus the value of phenylhydrazine as a reagent is not affected by Lipp's experiments.

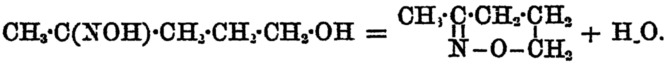
At the conclusion of his paper (*loc. cit.*, p. 1211), Lipp states that dihydromethylenefurfuran (methyldehydropentone) and trihydromethylenefurfuran (acetyltrimethylene) combine with phenylhydrazine, yielding the same substance as is obtained by the action of phenylhydrazine on acetopropyl alcohol. Lipp describes this latter substance (*loc. cit.*, p. 1203), the formation of which he explains by the equation



$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH + C_6H_5{\cdot}NH{\cdot}NH_2 = \left.\begin{array}{l}CH_3{\cdot}C{\cdot}CH_2{\cdot}CH_2\\ \quad\;\|\\ \quad\;N{\cdot}N(C_6H_5)\end{array}\right>CH_2 + 2H_2O,$$

as a reddish-brown oil, which, on exposure to the air, becomes dark reddish-brown, and ultimately resinifies; and he gives absolutely no proof that this uninviting product is identical with the similar reddish-brown oils which he obtained from methyldehydropentone and acetyltrimethylene by the action of phenylhydrazine. As from the nature of these substances it appeared to us that it would be scarcely possible, either directly or indirectly, to prove or disprove Lipp's statement, we carried out the analogous experiment with hydroxylamine instead of with phenylhydrazine.

Acetopropyl alcohol combines readily with hydroxylamine yielding an oxime, $CH_3{\cdot}C(:NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$; this oxime, when heated at 100°, is converted into its anhydride, thus :—

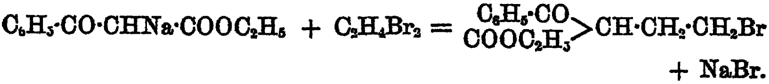


$$CH_3{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH = \begin{array}{l}CH_3{\cdot}C{\cdot}CH_2{\cdot}CH_2\\ \quad\;\| \qquad\quad |\\ \quad\;N-O-CH_2\end{array} + H_2O.$$

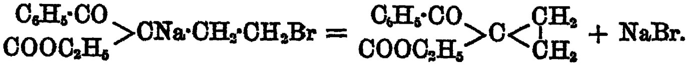
Now, this substance should, according to Lipp's argument, be identical with the oxime of acetyltrimethylene, if this latter compound is, as Lipp supposes, an anhydride of acetopropyl alcohol (methylenetetrahydrofurfuran), but as a fact the two differ entirely in their properties; the former is an oil, the latter a beautifully crystalline substance.

In carrying out this investigation of the acetyltrimethylene derivatives, we have also included a further study of the benzoyltrimethylene derivatives (Trans., 1885, **47**, 836—849; 1887, **51**, 837), in order to obtain further evidence to prove that these two series of compounds are analogously constituted.

It will be remembered that ethyl benzoyltrimethylenecarboxylate is produced by the action of sodium ethylate and ethylene bromide on ethyl benzoylacetate :—



$$C_6H_5{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + C_2H_4Br_2 = \left.\begin{array}{l}C_6H_5{\cdot}CO\\ COOC_2H_5\end{array}\right>CH{\cdot}CH_2{\cdot}CH_2Br + NaBr.$$

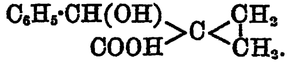


$$\left.\begin{array}{l}C_6H_5{\cdot}CO\\ COOC_2H_5\end{array}\right>CNa{\cdot}CH_2{\cdot}CH_2Br = \left.\begin{array}{l}C_6H_5{\cdot}CO\\ COOC_2H_5\end{array}\right>C<\begin{array}{l}CH_2\\ |\\ CH_2\end{array} + NaBr.$$

The following are the principal reactions of benzoyltrimethylenecarboxylic acid:—

1. It combines with hydroxylamine forming an oxime, $C_{11}H_{11}NO_3$.

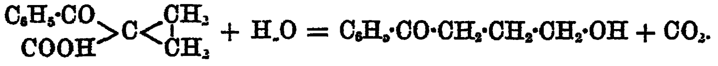
2. It is readily reduced by sodium amalgam with formation of hydroxybenzyltrimethylenecarboxylic acid,



$\begin{array}{r}C_6H_5\cdot CH(OH)\\ COOH\end{array}>C<\begin{array}{l}CH_2\\ |\\ CH_2\end{array}$.

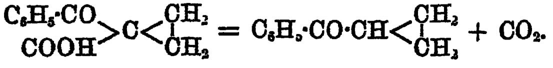
3. It is a saturated acid, and does not decolorise potassium permanganate in alkaline solution at ordinary temperatures even after standing for days.

4. When boiled with water, it is converted into benzoylpropyl alcohol:



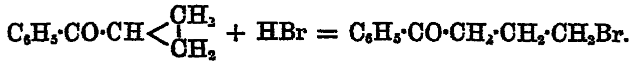
$$\begin{array}{r}C_6H_5\cdot CO\\ COOH\end{array}>C<\begin{array}{l}CH_2\\ |\\ CH_2\end{array} + H_2O = C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + CO_2.$$

5. On distillation, the acid yields benzoyltrimethylene with elimination of carbon dioxide:



$$\begin{array}{r}C_6H_5\cdot CO\\ COOH\end{array}>C<\begin{array}{l}CH_2\\ |\\ CH_2\end{array} = C_6H_5\cdot CO\cdot CH<\begin{array}{l}CH_2\\ |\\ CH_2\end{array} + CO_2.$$

Benzoyltrimethylene is a ketone, and as such it combines with hydroxylamine and phenylhydrazine. It dissolves readily in hydrobromic acid with formation of benzoylpropyl bromide:

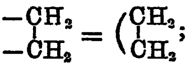


$$C_6H_5\cdot CO\cdot CH<\begin{array}{l}CH_2\\ |\\ CH_2\end{array} + HBr = C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2Br.$$

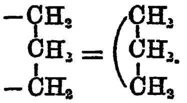
It will thus be seen that benzoyltrimethylenecarboxylic acid exactly resembles acetyltrimethylenecarboxylic acid in its reactions, and there can be no doubt the two acids are similarly constituted.

In following out this subject, it is, doubtless, somewhat difficult to accept the proposition that such simple reagents as hydrobromic acid, or such simple treatment as boiling with water or dilute acids, should be sufficient to split the trimethylene ring; and, again, it is remarkable that acetyltrimethylene and acetyltrimethylenecarboxylic acid should be reduced by powerful reducing agents, with disruption of the trimethylene ring; whereas the trimethylene di- and tri-carboxylic acids are not acted on even by a large excess of sodium amalgam.

These and other facts make it at once evident that the stability of the trimethylene ring in its derivatives depends very much on the nature and position of the substituting groups; thus, for instance, trimethylenedicarboxylic acid [1 : 2] and the tricarboxylic acid [1 : 2 : 3] are much more stable compounds than acetyltrimethylenecarboxylic acid or trimethylenedicarboxylic acid [1 : 1]. This is not remarkable when it is borne in mind that in the case of the ethylene derivatives, the stability of the ring is very different in various compounds; thus, for instance, ethylene and acrylic acid (ethylenecarboxylic acid) readily combine with bromine and hydrogen bromide, whereas fumaric acid (ethylenedicarboxylic acid) is only with difficulty attacked by these reagents, and similarly some ethylene compounds readily take up water when treated with dilute sulphuric acid or sodium hydrate, whereas others are not attacked under these conditions. It appears to us that the apparent difficulties, which operate against the general acceptance of the trimethylene formula, are readily explained on the assumption that ethylene and trimethylene compounds are analogously constituted; both hydrocarbons may be represented as possessing free affinities, which in the case of ethylene unite between 2 carbon atoms, in the case of trimethylene between 3 carbon atoms, thus:—



$$\begin{array}{l}-\mathrm{CH_2}\\ \;\;|\\ -\mathrm{CH_2}\end{array} = \left(\begin{array}{l}\mathrm{CH_2}\\ |\\ \mathrm{CH_2}\end{array}\right.;$$



$$\begin{array}{l}-\mathrm{CH_2}\\ \;\;|\\ \;\;\mathrm{CH_2}\\ \;\;|\\ -\mathrm{CH_2}\end{array} = \left(\begin{array}{l}\mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\end{array}\right..$$

Owing to the slight difference in constitution, it is natural to suppose that such substances would in general possess somewhat similar, though not identical, properties; and if this view be accepted, there will then be no difficulty in explaining any of the above-mentioned reactions.

Preparation of Acetyltrimethylenecarboxylic Acid, $\begin{array}{l}\mathrm{CH_2}\\ |\\ \mathrm{CH_2}\end{array}\!\!>\mathrm{C}<\!\begin{array}{l}\mathrm{CO{\cdot}CH_3}\\ \mathrm{COOH}\end{array}$.

The preparation of pure acetyltrimethylenecarboxylic acid is a matter of considerable difficulty, and as we required this substance in large quantities for subsequent experiments, it was thought necessary to work out some method by which the acid could be readily and rapidly purified. The following was ultimately found to give satisfactory results.

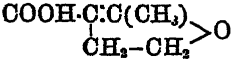
Crude acetyltrimethylenecarboxylic acid (prepared by the hydrolysis of the crude ethereal salt boiling between 185—200° (see Trans., 1887, **51**, 829) is dissolved in water (10 grams of acid in 200 c.c. of water) rendered distinctly alkaline by the addition of baryta-water, heated to boiling, and a stream of carbonic acid passed through the liquid until the excess of baryta has been converted into carbonate.

By this treatment all traces of colouring matter and other impurities are removed. and the filtrate from the barium carbonate is found to be perfectly colourless. This filtrate is evaporated to a small bulk, filtered if necessary, acidified with dilute hydrochloric acid, and repeatedly extracted with pure ether. The ethereal solution, after being dried over calcium chloride and evaporated, deposits a colourless oil. A sample of this was allowed to remain for three days over sulphuric acid in a vacuum and analysed, when it gave the following results:—

0·2671 gram substance gave 0·1551 gram H_2O and 0·5502 gram CO_2.

	Theory. $C_6H_8O_3$.	Found.
C......	56·25 per cent.	56·19 per cent.
H......	6·25 „	6·44 „
O......	37·50 „	37·37 „

These numbers agree well with those required for acetyltrimethylenecarboxylic acid, and the acid thus purified was used in most of the subsequent experiments.

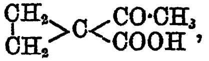
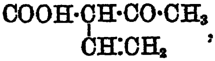
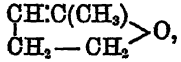
It is, nevertheless, obvious that any methyldehydropentonecarboxylic acid,  $\begin{matrix}\mathrm{COOH{\cdot}C{:}C(CH_3)}\\ |\qquad\qquad\quad\\ \mathrm{CH_2{-}CH_2}\end{matrix}\!>\!\mathrm{O}$ (see p. 878), which is present in the original crude acid. must also be contained in the above purified product, and for a considerable time great difficulty was experienced in getting rid of this impurity. Ultimately, oxidation with cold dilute alkaline potassium permanganate solution was found to produce the desired effect, as this reagent readily decomposes methyldehydropentonecarboxylic acid, leaving acetyltrimethylenecarboxylic acid unattacked.

5 grams of the purified acetyltrimethylenecarboxylic acid was dissolved in 200 c.c. of water, made slightly alkaline by the addition of potassium carbonate, and then a 1 per cent. solution of potassium permanganate added, drop by drop, the liquid being kept below 15° during the entire operation. At first the colour of the permanganate is rapidly destroyed, and the operation is continued until, after standing six hours, the liquid is still distinctly pink.

The excess of permanganate is then destroyed by the addition of alcohol, the product filtered, the clear solution evaporated to a small bulk, acidified with hydrochloric acid, and repeatedly extracted with pure ether. The ethereal solution was washed with a small quantity of salt solution, dried over calcium chloride, and the ether evaporated, when a colourless liquid was obtained, which, after standing over sulphuric acid in a vacuum, gave the following results on analysis:—

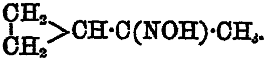
0·1370 gram substance gave 0·0812 gram H_2O and 0·2909 gram CO_2.

	Theory. $C_6H_8O_3$.	Found.
C	56·25 per cent.	55·91 per cent.
H	6·25 „	6·58 „
O	37·50 „	37·51 „

This acid is now completely free from methyldehydropentonecarboxylic acid, and appears to consist of practically pure acetyltrimethylenecarboxylic acid. Its most important property is that it is not affected by weak alkaline permanganate in the cold, a proof that the acid must be a saturated compound, as represented by the formula  $\begin{array}{c}CH_2\\|\\CH_2\end{array}\!>C<\!\begin{array}{l}CO\cdot CH_3\\COOH\end{array}$, and that it cannot be vinylacetoacetic acid,  $\begin{array}{l}COOH\cdot CH\cdot CO\cdot CH_3\\ \qquad\quad |\\ \qquad CH{:}CH_2\end{array}$, as suggested by Fittig (*Annalen*, **227**, 29), or methyldehydropentonecarboxylic acid,  $\begin{array}{l}CH{:}C(CH_3)\\|\\CH_2-CH_2\end{array}\!>O$, as suggested by Lipp (*Ber.*, **22**, 1210).

This important test for saturated compounds, which was devised by Baeyer (*Annalen*, **245**, 146), was, in the present case, carried out as follows:—2 drops of the acid were dissolved in an excess of a weak solution of potassium carbonate, in a test tube, and 1 drop of a weak permanganate solution added; the pink tint produced was permanent, even after standing for two days, whereas, if the acid had been unsaturated, the colour would, at once, have been discharged.

The properties of pure acetyltrimethylenecarboxylic acid are otherwise very similar to those of the crude acid previously described (Trans., 1885, **47**, 832).

Acetyltrimethyleneoxime,  $\begin{array}{c}CH_2\\|\\CH_2\end{array}\!>CH\cdot C(NOH)\cdot CH_3$.

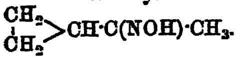
In some previous experiments on acetyltrimethylene (Trans., 1885, **47**, 835), it was stated that this substance combines with hydroxylamine to form a crystalline compound, probably an oxime; but this was not then analysed owing to lack of material. As, however, it was of great importance to establish the presence of a carbonyl group in acetyltrimethylene, these experiments were repeated on a larger scale, and a beautifully crystalline compound was obtained which, on examination, proved to be the desired oxime of acetyltrimethylene.

10 grams of pure acetyltrimethylene was dissolved in a little methyl alcohol, mixed with a concentrated aqueous solution of 12 grams of hydroxylamine hydrochloride, and a solution of 20 grams of pure potassium hydrate dissolved in methyl alcohol slowly run in,

the whole being well cooled during the operation. After standing for 24 hours, water was added, the alcohol driven off by gently warming on a water-bath, the solution rendered slightly acid by the addition of dilute hydrochloric acid, and the whole extracted several times with pure ether. The ethereal solution, when dried over calcium chloride and evaporated, deposited a colourless oil which, on standing over sulphuric acid in a vacuum, almost completely solidified. The crude product was freed from oily mother liquor by spreading it on a porous plate, and then recrystallised from benzene. The following results were obtained on analysis :—

0·1451 gram substance gave 0·1239 gram H_2O and 0·3237 gram CO_2.

0·1774 gram substance gave 23·2 c.c. N ; $t = 11°$; bar. $= 716$ mm.



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>CH{\cdot}C(NOH){\cdot}CH_3.$$

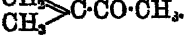
	Theory.	Found.
C......	60·60 per cent.	60·84 per cent.
H......	9·09 ,,	9·48 ,,
N......	14·14 ,,	14·60 ,,

Acetyltrimethyleneoxime melts at 50—51°. and when carefully heated distils without decomposition; the oily distillate solidifies completely on rubbing it with a glass rod.

It is readily soluble in water, alcohol, ether, chloroform, benzene, and light petroleum, and can be obtained in the form of magnificent, glistening prisms by allowing its concentrated solution in cold benzene to evaporate spontaneously.

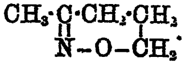
In an interesting paper on the decomposition of amylene nitrosate with sodium ethoxide (*Annalen*, **262**, 339—354), Wallach describes an oxime of the formula C_5H_9NO, which is isomeric with acetyltrimethyleneoxime. This oxime melts at 45°, and when heated with dilute sulphuric acid yields a new ketone, C_5H_8O, which boils at 98—102°.

From its method of formation, it is possible that this ketone, which is isomeric with acetyltrimethylene, has the constitution



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{\cdot}CO{\cdot}CH_3.$$

Oxime of Acetopropyl Alcohol, $CH_3{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, *and its Anhydride,*



$$\begin{matrix}CH_3{\cdot}C{\cdot}CH_2{\cdot}CH_2\\ \| \qquad\quad |\\ N-O-CH_2\end{matrix}.$$

In the course of this investigation it became necessary, for reasons stated in the introduction, to prove that the anhydride of the oxime of acetopropyl alcohol was not identical with the oxime of acetyltrimethylene (p. 866); and with this object in view we first prepared the oxime of acetopropyl alcohol.

3 grams of pure acetopropyl alcohol was dissolved in a little water, mixed with 3 grams of hydroxylamine hydrochloride, a moderately strong solution containing 5 grams of pure potassium hydrate added, and the whole allowed to remain at the ordinary temperature for three days. The product was then rendered slightly acid with hydrochloric acid, saturated with calcium chloride, and repeatedly extracted with ether; the ethereal solution was dried over calcium chloride, allowed to evaporate at the ordinary temperature, and the residual colourless oil left over sulphuric acid for four weeks.

The results obtained on analysis show that this substance is the oxime of acetopropyl alcohol:—

0·1935 gram substance gave 0·1659 gram H_2O and 0·3618 gram CO_2.

0·1660 gram substance gave 18·0 c.c. N; $t = 15°$; bar. = 726 mm.

	Theory. $C_5H_{11}NO_2$.	Found.
C	51·29 per cent.	51·00 per cent.
H	9·40 ,,	9·52 ,,
N	11·97 ,,	12·12 ,,

The oxime was readily converted into its anhydride by simply heating it on a watch glass at 100°.

The colourless, oily anhydride, which remained liquid even after standing over sulphuric acid in a vacuum for 14 days, gave on analysis the following numbers:—

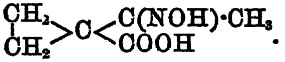
0·1527 gram substance gave 0·1267 gram H_2O and 0·3381 gram CO_2.

0·0780 gram substance gave 9·7 c.c. N; $t = 18°$; bar. = 746 mm.

	Theory. C_5H_9NO.	Found.
C	60·61 per cent.	60·39 per cent.
H	9·09 ,,	9·22 ,,
N	14·14 ,,	13·97 ,,

This anhydride is isomeric with acetyltrimethyleneoxime, which is crystalline, and melts at 50—51°.

Oxime of Acetyltrimethylenecarboxylic Acid,



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}>C<\begin{matrix}C(NOH)\cdot CH_3\\COOH\end{matrix}.$$

This interesting substance may be readily prepared in the following manner:—Acetyltrimethylenecarboxylic acid (1 mol.) is dissolved in a little water, mixed with a solution of pure potassium hydrate (4 mols.), and then a solution of hydroxylamine hydrochloride ($1\frac{1}{2}$ mols.) added, the temperature being kept below 30° during the operation. The product is allowed to stand for 24 hours, acidified with hydrochloric acid, the solution saturated with salt and repeatedly extracted with pure ether. The ethereal solution, after drying over calcium chloride, deposits the oxime, on evaporation, in beautiful, four-sided, tabular crystals.

The analysis of these crystals gave the following results:—

I. 0·2134 gram substance gave 0·1229 gram H_2O and 0·3933 gram CO_2.

0·2810 gram substance gave 23·2 c.c. N; $t = 15°$; bar. = 759 mm.

II. 0·1472 gram substance gave 0·0872 gram H_2O and 0·2714 gram CO_2.

0 2895 gram substance gave 24·4 c.c. N; $t = 12°$; bar. = 739 mm.

	Theory. $C_6H_9NO_3$.	Found. I.	Found. II.
C	50·36 per cent.	50·27	50·40 per cent.
H	6·29 ,,	6·40	6·58 ,,
N	9·78 ,,	9·84	9 69 ,,

This beautiful substance melts at about 157—158° with decomposition and rapid evolution of carbon dioxide. It dissolves readily in water, alcohol, and ether, but is only sparingly soluble in benzene, chloroform, and light petroleum.

In view of the interest which attaches to the formation of internal anhydrides in the oximes of β-ketonic acids (see below), the stability of the oxime of acetyltrimethylenecarboxylic acid was further tested by heating the substance at 100° for half an hour. At the end of this time the oxime was found to be wholly unchanged in appearance and melting point, and the following analysis shows that no formation of anhydride had taken place.

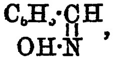
0·213 gram substance gave 18·5 c.c. N; $t = 17°$; bar. = 739 mm.

	Theory. $C_6H_9NO_3$.	Found.
N	9·78 per cent.	9·86 per cent.

Similar results were obtained with the oxime of benzoyltrimethylenecarboxylic acid (p. 883).

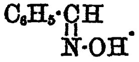
The formation and stability of the oximes of acetyltrimethylenecarboxylic acid and benzoyltrimethylenecarboxylic acid are extremely interesting in their relation to the recent work of Claisen (*Ber.*, **24**, 140) and of Hantzsch (*Ber.*, **24**, 495—506, and other papers) on the aldoximes and the oximes of ketonic acids.

Hantzsch explains the isomerism, so often observed in structurally identical oximes, such as in the case of benzaldoxime, $C_6H_5\cdot CH{:}NOH$, by assuming that these may exist in two stereochemical forms thus:—



$$\begin{array}{l} C_6H_5\cdot CH \\ \qquad\quad\;\| \\ \;\;OH\cdot N \end{array},$$

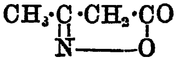
a-Aldoxime.



$$\begin{array}{l} C_6H_5\cdot CH \\ \qquad\quad\;\| \\ \qquad\quad N\cdot OH \end{array}.$$

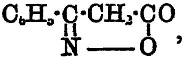
β-Aldoxime.

The oximes of *β*-ketonic acids, however, according to Hantzsch, never appear in two stereochemical forms, and, indeed, so far, these have never been obtained in the free state. Thus, ethyl acetoacetate, when treated with hydroxylamine, yields methylisoxalone, the internal anhydride of the oxime of acetoacetic acid,



$$CH_3\cdot C(NOH)\cdot CH_2\cdot COOH = \begin{array}{l} CH_3\cdot C\cdot CH_2\cdot CO \\ \qquad\;\;\| \qquad\quad\; | \\ \qquad\;\; N\text{———}O \end{array} + H_2O.$$

Similarly, benzoylacetic acid and hydroxylamine yield phenylisoxalone,

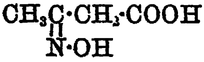


$$\begin{array}{l} C_6H_5\cdot C\cdot CH_2\cdot CO \\ \qquad\;\;\| \qquad\quad\; | \\ \qquad\;\; N\text{———}O \end{array},$$

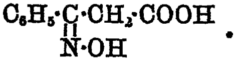
and not the free oxime,

$$C_6H_5\cdot C(NOH)\cdot CH_2\cdot COOH.$$

The formation of these anhydrides shows at once that the oximes of acetoacetic acid and of benzoylacetic acid have the *β*-configurations:

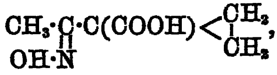


$$\begin{array}{l} CH_3C\cdot CH_2\cdot COOH \\ \qquad\;\| \\ \qquad N\cdot OH \end{array},$$

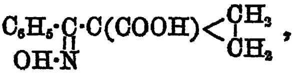


$$\begin{array}{l} C_6H_5\cdot C\cdot CH_2\cdot COOH \\ \qquad\quad\;\| \\ \qquad\quad N\cdot OH \end{array}.$$

The experiments on the oximes of acetyltrimethylenecarboxylic acid and of benzoyltrimethylenecarboxylic acid show conclusively that some of the oximes of *β*-ketonic acids, at all events, are capable of existing in the free state, and the fact that these oximes do not, even at 100°, yield internal anhydrides (isoxazolones) appears to show that these have the *a*-configuration,



$$\begin{array}{l} CH_3\cdot C\cdot C(COOH){<}\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array} \\ \qquad\;\| \\ OH\cdot N \end{array},$$

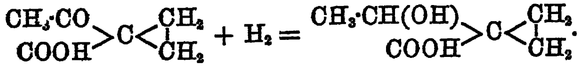


$$\begin{array}{l} C_6H_5\cdot C\cdot C(COOH){<}\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array} \\ \qquad\quad\;\| \\ \quad OH\cdot N \end{array},$$

and from the behaviour of these trimethylene derivatives, it seems probable that other disubstituted derivatives of ethyl acetoacetate and ethyl benzoylacetate may, when investigated, be found to yield *a*-oximes, and not isoxalones.

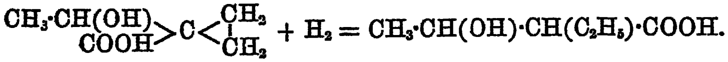
Reduction of Acetyltrimethylenecarboxylic Acid.

As stated in the introduction, acetyltrimethylenecarboxylic acid is readily reduced by sodium amalgam with formation, in the first place, of hydroxyethyltrimethylenecarboxylic acid:



$$\begin{matrix}CH_3{\cdot}CO\\COOH\end{matrix}{>}C{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix} + H_2 = \begin{matrix}CH_3{\cdot}CH(OH)\\COOH\end{matrix}{>}C{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix}.$$

If, however, a very large excess of sodium amalgam is employed, the ultimate product of the reaction is α-ethyl-β-hydroxybutyric acid, thus:—



$$\begin{matrix}CH_3{\cdot}CH(OH)\\COOH\end{matrix}{>}C{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix} + H_2 = CH_3{\cdot}CH(OH){\cdot}CH(C_2H_5){\cdot}COOH.$$

In studying this reduction, very carefully purified acetyltrimethylenecarboxylic acid was dissolved in water, neutralised with sodium carbonate, and reduced with nearly twice the calculated quantity of sodium amalgam (for H_2), added in small portions at a time. To promote thorough reduction, the vessel containing the sodium salt was constantly agitated, and the temperature prevented from rising by cooling externally by a stream of water.

As soon as the reduction was complete, the mercury was run off, the alkaline solution nearly neutralised with dilute hydrochloric acid, extracted with ether to remove a small quantity of a neutral substance which is always formed, acidified with hydrochloric acid, and extracted 10 times with pure ether.

The ethereal solution was dried over calcium chloride, evaporated, and the residual, almost colourless, oily acid, after standing over sulphuric acid in a vacuum for three days, analysed with the following result:—

0·1609 gram substance gave 0·1098 gram H_2O and 0·3296 gram CO_2.

0·1516 gram substance gave 0·1035 gram H_2O and 0·3089 gram CO_3.

	Theory. $C_6H_{10}O_3$.	Found. I.	 II.	
C	55·38 per cent.	55·80	55·59	per cent.
H	7·69 ,,	7·58	7·59	,,
O.......	36·92 ,,	36·62	36·82	,,

Hydroxyethyltrimethylenecarboxylic acid is a thick, strongly acid syrup miscible with water in all proportions. It distils with very slight decomposition if rapidly fractioned under reduced pressure (30 mm.).

A small quantity of the acid used in Analysis II was very rapidly distilled under a pressure of 30 mm., and two fractions, 175—180° and 180—185°, collected. The first of these gave, on analysis, the following numbers, showing that there had been only a very slight loss of water during the distillation:—

0·1780 gram substance gave 0·1176 gram H_2O and 0·3630 gram CO_2.

	Theory. $C_6H_{10}O_3$.	Found.
C	55·38 per cent.	55·75 per cent.
H	7·69 „	7·38 „
N	36·92 „	36·87 „

The distilled acid was a thick, perfectly colourless oil, soluble in water with only a faint turbidity.

In order to prepare the *silver salt* of this acid, the two fractions referred to above were separately dissolved in small quantities of water, neutralised carefully with potassium hydrate, and mixed with a slight excess of silver nitrate, dissolved in a very small quantity of water. It is necessary to have all the solutions concentrated in the above operation, otherwise the silver salt, which is readily soluble in water, is not precipitated. The white silver salt, was then collected, washed with a little water, dried on a porous plate, and recrystallised twice from boiling absolute alcohol; it was thus obtained in the form of microscopic needles, which, on analysis, gave the following numbers:—

I. Silver salt from fraction of acid boiling at 175—180° (30 mm.)—
0·3912 gram substance gave 0·4330 gram CO_2, 0·1412 gram H_2O, and 0·1784 gram Ag.

II. Silver salt from fraction of acid boiling at 180—185° (30 mm.)—
0·4162 gram substance gave 0·4641 gram CO_2, 0·1446 gram H_2O, and 0·1894 gram Ag.

	Theory.	Found.	
	$C_6H_9O_3Ag$.	I.	II.
C	30·38 per cent.	30·18	30·41 per cent.
H	3·80 „	4·01	3·86 „
Ag	45·58 „	45·61	45·50 „

The *copper salt* was obtained as a beautiful, green, crystalline mass, on adding a solution of copper sulphate to a strong, neutral solution of the potassium salt; it appears to contain 1 mol. H_2O:—

0·2714 gram substance gave, on ignition, 0·0682 gram of CuO.

	Theory. $(C_6H_9O_3)_2Cu + H_2O$.	Found.
Cu......	20·10 per cent.	20·06 per cent.

This copper salt is readily decomposed by heating above 90°, and, therefore, the amount of water of crystallisation could unfortunately not be determined.

The *lead, barium,* and *calcium salts* of hydroxyethyltrimethylenecarboxylic acid are readily soluble in water.

α-Ethyl-β-hydroxybutyric Acid.—In order to determine whether sodium amalgam had any further action on hydroxyethyltrimethylenecarboxylic acid, the following experiment was instituted:—

11 grams of pure acetyltrimethylenecarboxylic acid was dissolved in water, neutralised with sodium carbonate, and reduced by the gradual addition of 500 grams of 2½ per cent. sodium amalgam. The alkaline solution was neutralised with hydrochloric acid, evaporated to a small bulk, acidified, and the acid solution repeatedly extracted with ether. The ethereal solution was evaporated, the residual oily acid redissolved in sodium carbonate solution, and again treated with 500 grams of the amalgam. This operation was repeated a third time, and the ethereal solution of the ultimate product washed with a very little water, dried over calcium chloride, and evaporated.

The residual oily acid, after standing for some days over sulphuric acid in a vacuum, gave the following numbers on analysis:—

0·1748 gram substance gave 0·1440 gram H_2O and 0·3483 gram CO_2.

	Theory. $CH_3\cdot CH(OH)\cdot CH(C_2H_5)\cdot COOH$.	Found.
C........	54·54 per cent.	54·35 per cent.
H........	9·09 ,,	9·15 ,,
O........	36·36 ,,	36·50 ,,

These numbers agree well with those required for *α-ethyl-β-hydroxybutyric acid.* This acid has already been prepared by Wahlschmidt (*Annalen,* 188, 240) by the reduction of ethylic ethylacetoacetate with sodium amalgam:

$$CH_3\cdot CO\cdot CH(C_2H_5)\cdot COOC_2H_5 + H_2 + NaOH = CH_3\cdot CH(OH)\cdot CH(C_2H_5)\cdot COONa + C_2H_5\cdot OH.$$

It is described as a syrup which, when distilled, is converted into α-ethylcrotonic acid, thus:—

$$CH_3\cdot CH(OH)\cdot CH(C_2H_5)\cdot COOH = CH_3\cdot CH{:}C(C_2H_5)\cdot COOH + H_2O.$$

In order, therefore, to establish the identity of the acid obtained by the reduction of hydroxyethyltrimethylenecarboxylic acid with the α-ethyl-β-hydroxybutyric acid obtained by Wahlschmidt, it was only necessary to submit the former to distillation, and thus to obtain α-ethylcrotonic acid, which, being a crystalline and well characterised acid, could readily be identified.

The sample of acid, analysed above, was, therefore, carefully distilled from a small retort, the distillate returned to the retort, and again distilled, the operation being repeated until it appeared that all the hydroxy-acid had been decomposed. The distillate was then dissolved in water, neutralised with sodium hydrate, and the solution, after extracting with ether to remove traces of neutral compounds, precipitated with acetate of lead. The white, crystalline lead salt, thus obtained, was purified by recrystallisation from water, the pure salt decomposed by hydrochloric acid, and the strongly-smelling, oily acid which separated extracted with ether. The ethereal solution was dried over calcium chloride and allowed to evaporate spontaneously, when a quantity of four-sided prisms separated out. The crystals melted at 38°, and showed all the properties of α-ethylcrotonic acid. Analysis :—

0·1320 gram substance gave 0·1051 gram H_2O and 0 3048 gram CO_2.

	Theory. $CH_3\cdot CH\!:\!C(C_2H_5)\cdot COOH$.	Found.
C	63·16 per cent.	62·98 per cent.
H.......	8·77 „	8·85 „
O	28·07 „	28 17 „

In order to further establish the identity of this acid, the pure crystalline substance was dissolved in a slight excess of dilute sodium hydrate solution, which was then carefully neutralised with dilute nitric acid, heated to boiling, mixed with an excess of silver nitrate, and filtered. The solution, on cooling, deposited beautiful, white, glistening plates of silver α-ethylcrotonate.

The analysis of this salt gave the following result :—

0·2206 gram salt, on ignition, gave 0·1070 gram Ag.

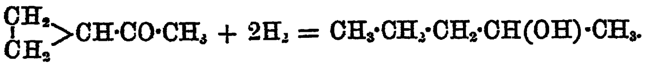
	Theory. $CH_3\cdot CH\!:\!C(C_2H_5)\cdot COOAg$.	Found.
Ag.....	48·87 per cent.	48·50 per cent.

These experiments prove, therefore, that the ultimate product of the action of sodium amalgam on acetyltrimethylenecarboxylic acid is *α-ethyl-β-hydroxybutyric acid.*

Reduction of Acetyltrimethylene.

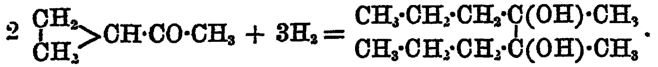
Formation of Methylpropylcarbinol.

When reduced by means of sodium in moist ethereal solution, acetyltrimethylene takes up 4 atoms of hydrogen with formation of methylpropylcarbinol, thus:—



$$\left.\begin{array}{l}CH_2\\ \,|\\ CH_2\end{array}\right>CH\cdot CO\cdot CH_3 + 2H_2 = CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH_3.$$

At the same time a considerable quantity of a substance of high boiling point is produced which, on examination, proved to be dimethyl dipropyl glycol. This substance is probably formed thus:—



$$2\left.\begin{array}{l}CH_2\\ \,|\\ CH_2\end{array}\right>CH\cdot CO\cdot CH_3 + 3H_2 = \begin{array}{l}CH_3\cdot CH_2\cdot CH_2\cdot C(OH)\cdot CH_3\\ \qquad\qquad\qquad\;\;|\\ CH_3\cdot CH_2\cdot CH_2\cdot C(OH)\cdot CH_3\end{array}.$$

The reduction was carried out as follows:—

15 grams of acetyltrimethylene was dissolved in 200 c.c. of ether, the solution floated on water, in a stout bottle connected with a reflux apparatus, and then 30 grams of sodium gradually added in small quantities at a time, the temperature being kept below 30° by sinking the bottle in water. As soon as the sodium had completely dissolved, the ethereal solution was separated, washed with a little water, dried over anhydrous potassium carbonate, and the ether slowly distilled off. The resulting, colourless, oily liquid was distilled, and thus readily separated into two principal fractions, about two-thirds passing over between 118° and 122° and the remainder between 210° and 230°. The lower fraction, on repeated fractionation, distilled constantly at 119·5°, and on analysis gave numbers agreeing with those required for methylpropylcarbinol, thus:—

0·1102 gram substance gave 0·2760 gram CO_2 and 0·1366 gram H_2O.

	Theory. $CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH_3$.	Found.
C	68·18 per cent.	68·30 per cent.
H	13·64 „	13·77 „
O	18·18 „	17·93 „

Methylpropylcarbinol has been prepared by Friedel (*Jahresbericht*, 1869, 513) from methyl propyl ketone and sodium amalgam, and by Markownikow (*J. Russ. Chem. Soc.*, 15, 407) from zinc propyl and acetyl chloride. It boils at 118·5° under a pressure of 753·2 mm., and possesses properties exactly similar to those observed in our preparation.

In order to further establish the identity of the methylpropylcarbinol obtained from acetyltrimethylene, it was converted into its acetate by digestion with excess of acetic anhydride for two hours in a reflux apparatus. The product was then shaken up with cold water until the excess of acetic anhydride had been decomposed, the oily acetate extracted with ether, the ethereal solution washed with dilute sodium carbonate solution, and dried over calcium chloride; on evaporating the ether and distilling the residue, the whole passed over between 132° and 134°, and, on refractioning, the acetate was obtained pure as a colourless liquid boiling at 133·5°. The analysis gave the following results:—

0·1499 gram substance gave 0·1459 gram H_2O and 0·3539 gram CO_2.

	Theory. $CH_3{\cdot}CH(C_2H_3O_2){\cdot}C_3H_7$.	Found.
C	64·61 per cent.	64·38 per cent.
H......	10·77 „	10·81 „
O	24·62 „	24·81 „

The boiling point of this acetate is variously given as:—133—135° (Würtz, *Annalen*, **148**, 132); 130—135° (Friedel, *Zeit. fur Chem.*, 1869, 476); 134—137° (Schorlemmer, *Annalen*, **161**, 269); these boiling points agree well with that found for the product from acetyltrimethylene.

Dimethyl Dipropyl Glycol.—The portion of the reduction product of acetyltrimethylene boiling at 210—230° was submitted to very careful fractionation in a Würtz flask with a long neck, and in this way a quantity of a thick, colourless oil was obtained boiling at 220—225°.

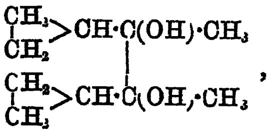
On analysis, it gave the following numbers:—

0·1142 gram substance gave 0·2881 gram CO_2 and 0·1282 gram H_2O.

	Theory. $C_3H_7{\cdot}C(OH){\cdot}CH_3$ $C_3H_7{\cdot}C(OH){\cdot}CH_3$.	Found.
C	68·96 per cent.	68·81 per cent.
H......	12·65 „	12·48 „
O	18·38 „	18·71 „

This substance appears to be identical with the methyl propyl pinacone obtained by Friedel (*Jahresbericht*, 1869, 513) by the reduction of methyl propyl ketone with sodium and water, and which this chemist found also to boil at 220—225°.

It was at first thought that this compound was ditrimethylene dimethyl glycol,

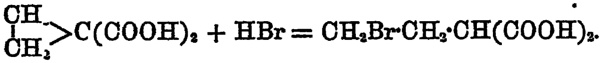


$$\begin{array}{l} {CH_2 \atop CH_2}\!>\!CH{\cdot}C(OH){\cdot}CH_3 \\ \qquad\qquad\quad | \\ {CH_2 \atop CH_2}\!>\!CH{\cdot}C(OH){\cdot}CH_3 \end{array},$$

the formation of which could be readily understood; but this glycol contains C = 70·58 : H = 10·58 per cent. instead of C = 68·81 : H = 12·48, found above.

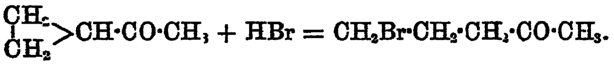
Action of Hydrogen Bromide on Acetyltrimethylene.

One of the most remarkable properties of trimethylenedicarboxylic acid is the ease with which it combines with hydrogen bromide, with formation of ω-bromethylmalonic acid, thus:—



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C(COOH)_2 + HBr = CH_2Br{\cdot}CH_2{\cdot}CH(COOH)_2.$$

When subjected to the same treatment, acetyltrimethylene undergoes a perfectly similar decomposition, being converted into acetopropyl bromide, thus:—



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>CH{\cdot}CO{\cdot}CH_3 + HBr = CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3.$$

In studying this interesting decomposition, 10 grams of pure acetyltrimethylene was added gradually to three times the volume of fuming hydrobromic acid (sp. gr. 1·83), care being taken to keep the temperature below 40°. After standing for 24 hours, the brownish solution was poured into water, the heavy oil which was deposited extracted twice with ether, and the ethereal solution washed with water, and dried over calcium chloride. On distilling off the ether, a brownish oil was obtained, which, on fractionation, boiled constantly at 120° under a pressure of 90 mm.

A bromine determination gave the following result, agreeing with that required for acetopropyl bromide:—

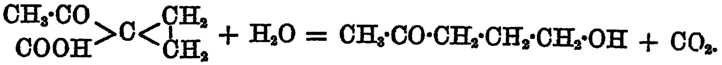
0·2134 gram substance, heated in a sealed tube with nitric acid and nitrate of silver, gave 0·2442 gram AgBr.

	Theory $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$.	Found.
Br.......	48·50 per cent.	48·70 per cent.

Acetopropyl bromide has already been prepared by Colman and Perkin (Trans., 55, 357) and by Lipp (*Ber.*, 22, 1206) from acetopropyl alcohol and hydrobromic acid, and a careful comparison of the bromide from acetyltrimethylene with that obtained from acetopropyl alcohol showed that the two products were identical.

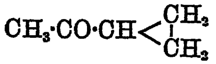
Hydrolysis of Acetyltrimethylene.

One of the most interesting reactions of acetyltrimethylenecarboxylic acid is the decomposition which it undergoes on prolonged boiling with water, whereby it is resolved apparently quantitatively into acetopropyl alcohol and carbon dioxide (Trans., 51, 829; 55, 357), thus:—



$$\begin{matrix}CH_3{\cdot}CO\\COOH\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\|\\CH_2\end{matrix} + H_2O = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH + CO_2.$$

In order to determine whether acetyltrimethylene,

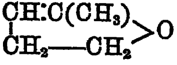


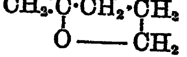
$$CH_3{\cdot}CO{\cdot}CH\!<\!\begin{matrix}CH_2\\|\\CH_2\end{matrix}$$

(which is obtained from the above acid by the elimination of carbon dioxide), would be hydrolysed by water, a number of experiments carefully conducted under different conditions were instituted.

A quantity of pure acetyltrimethylene (b. p. 112—113°) was dissolved in water, and the solution allowed to stand at the ordinary temperature for two weeks; anhydrous potassium carbonate was then added, the oily layer which separated extracted with ether, dried over calcium chloride, and the residue which remained after distilling off the ether carefully fractioned in a Würtz flask fitted with a long neck. The whole distilled between 110° and 115°, leaving no appreciable residue, thus showing that water at ordinary temperatures has no action on acetyltrimethylene.

In the second experiment, acetyltrimethylene was heated with four times its volume of water in a sealed tube at 100° for two days, and the product treated as above; in this case also, practically, the whole of the acetyltrimethylene was recovered unchanged. Experiments subsequently made showed that acetyltrimethylene is not hydrolysed even when heated with water for two days at 130° or for 12 hours at 200°.

This fact is very interesting as demonstrating the remarkable difference in stability between acetyltrimethylene and its isomer, *methyldehydropentone*,  $\begin{matrix}CH{:}C(CH_3)\\|\qquad\quad\\CH_2{-\!\!-}CH_2\end{matrix}\!>\!O$ (see p. 880), as the latter, in contact with water at ordinary temperature, is rapidly converted into acetopropyl alcohol (p. 882).

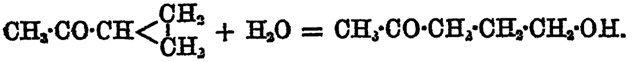
In a research on acetopropyl alcohol, Lipp (*Ber.*, 22, 1192) states that his so-called trihydromethylenefurfuran,  $\begin{matrix}CH_2{:}C{\cdot}CH_2{\cdot}CH_2\\\;\;|\qquad\quad|\\\;\;O{-\!\!-\!\!-}CH_2\end{matrix}$ (which boils at 110—111°, and is in all probability identical with acetyltrimethylene), when heated in a sealed tube with 5 per cent. hydrochloric acid at 100°, is converted into acetopropyl alcohol. As acetyltrimethylene is not hydrolysed by water alone, it was thought interesting to study its behaviour with 5 per cent. hydrochloric acid under the conditions employed by Lipp.

For this purpose, 20 grams of pure acetyltrimethylene was heated in a sealed tube with six times its volume of 5 per cent. hydrochloric acid for one hour at 100°, the product saturated with potassium carbonate, and then repeatedly extracted with pure ether. This ethereal solution, after drying over anhydrous potassium carbonate and evaporating, deposited an oil which, on distillation under reduced pressure (100 mm.), boiled between 140° and 150°, and on repeated fractionation, the greater portion passed over between 144 and 146°, and gave the following numbers on analysis :—

0·1598 gram substance gave 0·1397 gram H_2O and 0·3450 gram CO_2.

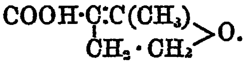
	Theory. $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$.	Found.
C	58 82 per cent.	59·05 per cent.
H	9·81 „	9·71 „
O	31·37 „	31·24 „

This experiment shows, therefore, that acetyltrimethylene, although not appreciably attacked by heating with water even at 200°, is readily hydrolysed by dilute hydrochloric acid at 100° with formation of acetopropyl alcohol, thus :—



$$CH_3\cdot CO\cdot CH<\begin{matrix}CH_2\\ | \\ CH_2\end{matrix} + H_2O = CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH.$$

Methyldehydropentonecarboxylic Acid,



$$\begin{matrix}COOH\cdot C{:}C(CH_3)\\ | \\ CH_2\cdot CH_2\end{matrix}>O.$$

This acid is apparently always present in the crude acetyltrimethylenecarboxylic acid prepared by hydrolysing the ethereal salt boiling between 180° and 210°, obtained as the principal product in the action of ethylene bromide on ethyl sodacetoacetate. The amount of methyldehydropentonecarboxylic acid present in this product appears to vary very considerably, and in spite of repeated experiments, we have only on one occasion been successful in obtaining this beautiful substance in any quantity in a pure condition.

The conditions employed in this experiment were approximately the following :—

During the preparation of very large quantities of ethyl acetyltrimethylenecarboxylate, a quantity of crude ethylene bromide and ethyl acetoacetate had been recovered as a fraction boiling between 120° and 185°, and weighing considerably over 1 kilo. This was fractioned once or twice, and thus separated into two principal fractions, boiling respectively at 130—150° and 170—185°. The former was considered to consist for the most part of ethylene bromide; the latter contained large quantities of ethyl acetoacetate. These crude products were employed in preparing a fresh quantity of ethyl acetyltrimethylenecarboxylate, the actual amounts which came into operation being 560 grams of ethyl acetoacetate, 400 grams of ethylene bromide, 100 grams of sodium, and about 1200 grams of absolute alcohol.

The mixture prepared in the usual way (Trans., 1885, **47**, 829) was heated for five hours in a reflux apparatus, the alcohol distilled off as completely as possible, the residue mixed with water, and the oily ethereal salt extracted with ether. The oily residue obtained after distilling off the ether was then subjected to distillation in a rapid current of steam till no more oily drops came over with the condensed water, the distillate extracted with ether, and the ethereal solution dried over calcium chloride and evaporated. The residue was fractioned, and the portion boiling between 170° and 230° hydrolysed by boiling in a reflux apparatus with an alcoholic solution of 30 grams of potassium hydrate for four hours. The alcohol was distilled off, and the residue diluted with water and evaporated to a small bulk on a water-bath.

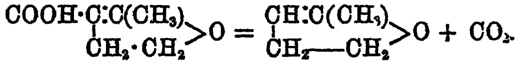
On standing, the liquid deposited beautiful, glistening plates of a potassium salt, which were dissolved by the addition of water, and the alkaline liquid acidified by hydrochloric acid, when a fine, white, crystalline mass was deposited. The crystals, which are very sparingly soluble in the salt solution, were collected, washed with a very little water, dried on a porous plate, and purified by recrystallisation from benzene. In this way the new acid was readily obtained pure in the form of brilliant, four-sided plates, which on analysis gave the following numbers:—

I. 0·1470 gram substance gave 0·0872 gram H_2O and 0·3041 gram CO_2.

II. 0·1614 gram substance gave 0·0922 gram H_2O and 0·3331 gram CO_2.

	Theory.	Found.	
	$C_6H_8O_3$.	I.	II.
C......	56·25 per cent.	56·41	56·28 per cent.
H......	6·25 "	6·59	6·34 "
O......	37·50 "	37·00	37·38 "

Methyldehydropentonecarboxylic acid melts at 150°, and at the same time decomposes into methyldehydropentone and carbon dioxide:



$$\begin{array}{l}COOH\cdot C{:}C(CH_3)\\ \quad\;\; CH_2\cdot CH_2\end{array}\!\!>O = \begin{array}{l}CH{:}C(CH_3)\\ CH_2{-}{-}CH_2\end{array}\!\!>O + CO_2.$$

When heated carefully in a current of an indifferent gas, this acid sublimes in the form of feathery crystals, with only slight decomposition.

It is readily soluble in warm water, ether, alcohol, and benzene, but only sparingly in light petroleum and cold water. The solution in hot water deposits the acid in colourless needles, on cooling, but if the solution is boiled, rapid decomposition sets in, with evolution of carbon dioxide and formation of an oily neutral substance, which is obviously acetopropyl alcohol.

The basicity of methyldehydropentonecarboxylic acid was determined by titrating a known quantity of the pure acid with a standard solution of potassium hydrate.

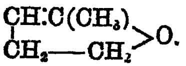
0·4500 gram of acid required for neutralisation 35·4 c.c. of potassium hydrate solution (1 c.c. = 0·00559 gram KOH) = 0·1978 gram KOH.

A monobasic acid of the formula $C_6H_8O_3$ requires 0·1950 gram KOH.

Methyldehydropentonecarboxylic acid differs from acetyltrimethylenecarboxylic acid very widely in its behaviour towards potassium permanganate. If a trace of the former acid is dissolved in a slight excess of dilute sodium carbonate solution, and a drop of permanganate solution added, the colour instantly disappears, and successive drops continue to be decolorised, until the acid is completely destroyed; acetyltrimethylenecarboxylic acid, on the contrary, does not decolorise permanganate solution.

Again, acetyltrimethylenecarboxylic acid, being a ketonic acid, reacts readily with hydroxylamine, yielding an oxime; methyldehydropentonecarboxylic acid is, on the other hand, not acted on by hydroxylamine. In order to prove this, 2 grams of the latter acid was dissolved in dilute potassium hydrate solution (containing 4 grams KOH), a solution of hydroxylamine hydrochloride (2 grams) added, and the whole allowed to stand for 24 hours. The aqueous solution was then concentrated, cooled well, acidified with hydrochloric acid, and the precipitate which separated collected, washed with a little water, and spread on a porous plate. The crystals, which weighed upwards of 1·7 grams and were free from nitrogen, were crystallised from benzene, and found to consist of unchanged methyldehydropentonecarboxylic acid.

Methyldehydropentone,



$$\begin{array}{l}CH{:}C(CH_3) \\ |\\ CH_2—CH_2\end{array}\!\!>O.$$

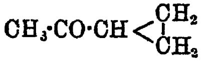
When heated above its melting point, methyldehydropentonecarboxylic acid is rapidly decomposed with evolution of carbon dioxide and formation of methyldehydropentone. In order to obtain this very interesting substance in quantity, 20 grams of the pure dry acid was gently heated in a small retort placed in an oil-bath and connected with a well-cooled condenser, the distillate being collected in a small flask cooled by means of a freezing mixture. The limpid, ethereal-smelling oil thus obtained, on subsequent fractionation, boiled constantly at 82°, and consisted of pure methyldehydropentone. Analysis:—

I. 0·1311 gram substance gave 0·1171 gram H_2O and 0·3442 gram CO_2.

II. 0·0881 gram substance gave 0·0781 gram H_2O and 0·2295 gram CO_2.

	Theory. C_5H_8O.	Found. I.	Found. II.
C	71·42 per cent.	71·60	71·07 per cent.
H	9·52 „	9·67	9·85 „
O	19·05 „	18·73	19·08 „

Methyldehydropentone is isomeric with acetyltrimethylene,



$CH_3{\cdot}CO{\cdot}CH{<}\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$ (b. p. 112°).

The specific gravity and magnetic rotation determinations of this substance, which were made by W. H. Perkin, sen., gave the following numbers:—

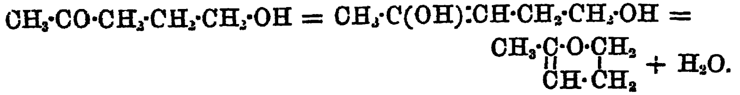
Density:—$d\,4°/4° = 0·9217$; $d\,10°/10° = 0·9154$; $d\,15°/15° = 0·9107$; $d\,20°/20° = 0·9062$; $d\,25°/25° = 0·9018$.

Magnetic Rotations.

	t.	Sp. rotation.	Mol. rotation.
	17·0°	1·0552	5·417
	17·0	1·0521	5·402
	17·0	1·0477	5·379
	17·4	1·0462	5·374
	17·8	1·0492	5·391
	14·3	1·0506	5·379
	12·7	1·0551	5·393
	12·8	1·0560	5·398
	12·0	1·0553	5·390
Average ..	15·3	1·0519	5·391

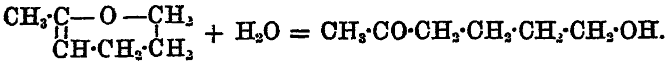
Action of Water on Methyldehydropentone. Formation of Acetopropyl Alcohol.

The formula given above to methyldehydropentone represents this substance as the anhydride of acetopropyl alcohol,



$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH = CH_3{\cdot}C(OH){:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH = \begin{array}{l} CH_3{\cdot}C{\cdot}O{\cdot}CH_2 \\ \quad\; \| \qquad\;\; | \\ \quad\; CH{\cdot}CH_2 \end{array} + H_2O.$$

It was, therefore, to be expected that this anhydride, when treated with water, would be converted into acetopropyl alcohol, just as methyldehydrohexone in contact with water is converted into acetobutyl alcohol (Trans., 1887, 51, 724),



$$\begin{array}{l} CH_3{\cdot}C{-}O{-}CH_2 \\ \quad\; \| \qquad\quad | \\ \quad\; CH{\cdot}CH_2{\cdot}CH_2 \end{array} + H_2O = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH.$$

10 grams of methyldehydropentone and 50 c.c. of water were placed in a stoppered bottle and kept at the ordinary temperature for some days. The oily layer which floated on the top of the water gradually became less and less, and ultimately entirely disappeared; the reaction is much hastened by agitating and gently warming the bottle from time to time. The clear solution thus obtained was saturated with potassium carbonate, extracted 20 times with pure ether, the ethereal solution dried over potassium carbonate, evaporated, and the residual oil purified by distillation under reduced pressure (80 mm.). In this way a colourless oil was obtained, which boiled constantly at 139° and gave the following numbers on analysis:—

0·1548 gram substance gave 0·1388 gram H_2O and 0·3360 gram CO_2.

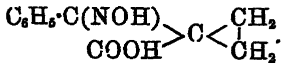
	Theory. $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.	Found.
C	58·82 per cent.	59·19 per cent.
H	9·81 „	9·96 „
O	31·37 „	30·85 „

The substance produced by the action of water on methyldehydropentone is, therefore, acetopropyl alcohol, and in this respect methyldehydropentone differs widely from the isomeric acetyltrimethylene, which, as was shown on p. 877, is not acted on by water even at moderately high temperatures.

In a previous investigation of the products of the distillation of crude acetyltrimethylenecarboxylic acid (which, as has already been shown, always contains methyldehydropentonecarboxylic acid), a small quantity of a substance was obtained boiling at 85—95°, which, when dissolved in water, was converted into acetopropyl alcohol, and which, therefore, undoubtedly consisted of slightly impure methyldehydropentone (Trans., 1887, 51, 831).

Lipp (*Ber.*, 22, 1199) also described a substance boiling at 72—75°, which he obtained by distilling acetopropyl alcohol, and which should therefore be the anhydride of the alcohol. It is probable that this substance, which, however, Lipp, curiously enough, describes as unstable, consisted of impure methyldehydropentone.

Oxime of Benzoyltrimethylenecarboxylic Acid,



$$\begin{matrix} C_6H_5\cdot C(NOH) \\ COOH \end{matrix} > C < \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}.$$

With the object of proving the ketonic nature of benzoyltrimethylenecarboxylic acid, and, at the same time, of demonstrating the similarity in constitution between this acid and acetyltrimethylenecarboxylic acid, experiments on the behaviour of this acid towards hydroxylamine were instituted. 1·9 grams of pure benzoyltrimethylenecarboxylic acid was dissolved in a dilute solution of potassium hydrate containing 2·2 grams of KOH; 1 gram of hydroxylamine hydrochloride in solution was added, and the mixture allowed to stand for 24 hours. The clear alkaline solution was acidified with hydrochloric acid, the sticky, semi-solid mass, which, on stirring with a glass rod, became quite solid, collected, washed with water, and dried on a porous plate. It was then ground up, extracted with a little boiling benzene to remove any unchanged benzoyltrimethylenecarboxylic acid and other impurities, and recrystallised from water. In this way thick, colourless prisms were obtained, which, on analysis, gave the following numbers:—

0·1474 gram substance gave 0·0768 gram H_2O and 0·3467 gram CO_2.

0·1436 gram substance gave 8·2 c.c. N; $t = 20°$; bar. = 755 mm.

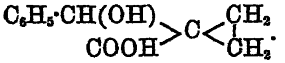
	Theory. $C_{11}H_{11}NO_3$.	Found.
C	64·39 per cent.	64·15 per cent.
H	5·37 „	5·79 „
N	6·83 „	6·64 „

When heated in a capillary tube, the oxime softens at 160° and melts fairly sharply at about 164—166° with decomposition. The crystalline substance is readily soluble in alcohol and warm water, very readily in acetic acid, but only very sparingly in benzene, light petroleum, and chloroform.

The oxime of benzoyltrimethylenecarboxylic acid does not yield an anhydride, even on heating at 100° for one hour (compare pp. 868—869).

Reduction of Benzoyltrimethylenecarboxylic Acid.

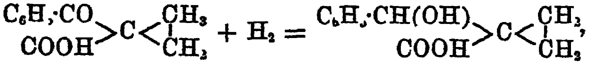
Formation of Hydroxybenzyltrimethylenecarboxylic Acid,



$$\begin{matrix}C_6H_5\cdot CH(OH)\\ COOH\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}.$$

When subjected to the action of sodium amalgam, acetyl trimethylenecarboxylic acid is readily reduced with formation of hydroxyethyltrimethylenecarboxylic acid, and this acid, under the influence of a large excess of sodium amalgam, is ultimately reduced to α-ethyl-β-hydroxybutyric acid (see pp. 870 and 872).

The constitution of benzoyltrimethylenecarboxylic acid being analogous to that of acetyltrimethylenecarboxylic acid, it yields under similar circumstances hydroxybenzyltrimethylenecarboxylic acid,



$$\begin{matrix}C_6H_5\cdot CO\\ COOH\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + H_2 = \begin{matrix}C_6H_5\cdot CH(OH)\\ COOH\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix},$$

but whether this acid, on treatment with excess of sodium amalgam, can be converted into hydroxybenzylethylacetic acid,

$$C_6H_5\cdot CH(OH)\cdot CH\cdot(C_2H_5)\cdot COOH,$$

has not yet been definitely established. In studying this reduction, pure benzoyltrimethylenecarboxylic acid was dissolved in dilute sodium hydrate solution, and the sodium salt treated in a flat porcelain dish with about 1½ times the calculated quantity of 2½ per cent. sodium amalgam.

During the operation a white, crystalline sodium salt separated, which greatly impeded the reduction, and, therefore, especially at the latter part of the experiment, it was found necessary to bring this salt into solution by maintaining the liquid at a temperature of from 50—60°, with the occasional addition of small quantities of water The product, after being separated from the mercury, was filtered hot, acidified with dilute sulphuric acid, and several times extracted with ether. The ethereal solution, when dried over calcium chloride and evaporated, deposited a colourless oil, which rapidly and completely solidified on standing. The crystalline cake was purified first by recrystallisation from a mixture of benzene and light petroleum; the crystals were then dissolved in a small quantity of hot water, the solution filtered, and vigorously stirred as it cooled to prevent the formation of oily drops. In this way the new acid was obtained in the form of glistening, four-sided plates, which on analysis gave the following numbers:—

I. 0·1688 gram substance gave 0·0972 gram H_2O and 0·4238 gram CO_2.

II. 0·1472 gram substance gave 0·0868 gram H_2O and 0·3705 gram CO_2.

	Theory. $C_{11}H_{12}O_3$.	Found. I.	Found. II.
C	68·75 per cent.	68·49	68·57 per cent.
H	6·25 „	6 39	6·55 „
O	25·00 „	25·22	24·88 „

Hydroxybenzyltrimethylenecarboxylic acid melts at 94—96°. It is readily soluble in benzene, alcohol, and ether, but only moderately so in hot and sparingly in cold water.

The solution of the acid in dilute sodium carbonate does not decolorise potassium permanganate, even on standing for some time. When distilled, the acid is decomposed into water and a yellow oil. This oil appears to consist for the most part of two substances boiling at about 180—200° and 265—270° (140 mm.). The lower fraction smelt strongly of cinnamene, and the higher fraction on long standing solidified, but owing to the small quantities of these fractions at our disposal no clue to their constitution was obtained.

Salts of Hydroxybenzyltrimethylenecarboxylic Acid.

The *silver salt*, $C_{11}H_{11}AgO_3$, was prepared by precipitating a neutral solution of the ammonium salt with silver nitrate. The white, amorphous salt thus obtained was washed with water, dried on a porous plate over sulphuric acid in a vacuum, and analysed with the following result:—

0·2522 gram substance gave 0·0898 gram Ag.

	Theory. $C_{11}H_{11}AgO_3$.	Found.
Ag	36·03 per cent.	35·61 per cent.

A dilute neutral solution of the ammonium salt shows the following behaviour with reagents:—

Copper sulphate, a light blue precipitate, sparingly soluble in water. *Lead acetate*, a white, caseous precipitate, moderately soluble in hot water. *Zinc sulphate*, a white precipitate, soluble in hot water. *Barium chloride* and *calcium chloride*, no precipitate.

Reduction of Benzoyltrimethylene.

Formation of Phenylpropylcarbinol, $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$.

The reduction of acetyltrimethylene to methylpropylcarbinol by means of sodium in moist ethereal solution is described on p. 874;

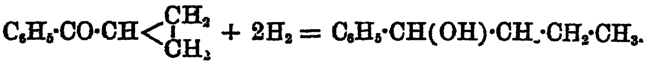
and, in studying this curious result, it appeared to us that it would be interesting to investigate the action of this reducing agent on benzoyltrimethylene, in order to determine whether both these ketones would behave in the same way under this treatment.

About 10 grams of pure benzoyltrimethylene dissolved in pure ether was floated on water, and reduced by 40 grams of sodium in small quantities at a time, the experiment being conducted exactly as in the case of the reduction of acetyltrimethylene. As soon as all the sodium had dissolved the ethereal solution was separated, washed with a little water, dried over calcium chloride, evaporated, and the coloured, oily residue purified by fractionation under reduced pressure (100 mm.). About half of the substance distilled between 165° and 175°, leaving a thick, oily residue, which did not distil without decomposition, and was, therefore, not further examined. The fraction 165—175°, on redistillation, passed over almost entirely between 168° and 170 (under a pressure of 100 mm.), and gave on analysis the following numbers:—

0·1589 gram substance gave 0·1246 gram H_2O and 0·4671 gram CO_2.

	Theory. $C_6H_5{\cdot}CH(OH){\cdot}C_3H_7$.	Found.
C	80·00 per cent.	80·12 per cent.
H	9·33 „	9·33 „
O	10·66 „	10·55 „

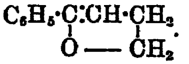
The substance is obviously phenylpropylcarbinol, produced by the addition of 4 atoms of hydrogen to benzoyltrimethylene, thus:—



$$C_6H_5{\cdot}CO{\cdot}CH{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix} + 2H_2 = C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_3.$$

Phenylpropylcarbinol is a thick, colourless oil, of powerful aromatic odour, somewhat resembling that of benzyl alcohol.

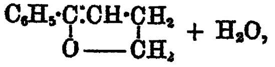
Benzoylpropyl Alcohol, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, *and* *Phenyldehydropentone*,



$$\begin{array}{l} C_6H_5{\cdot}C{:}CH{\cdot}CH_2 \\ \qquad\;\; | \qquad\quad | \\ \qquad\;\; O \;\text{———}\; CH_2 \end{array}.$$

Unlike acetopropyl alcohol, benzoylpropyl alcohol is only theoretically capable of forming one internal anhydride, thus:—

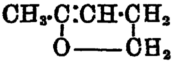
$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH = C_6H_5{\cdot}C(OH){:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH =$$



$$\begin{array}{l} C_6H_5{\cdot}C{:}CH{\cdot}CH_2 \\ \qquad\;\; | \qquad\quad | \\ \qquad\;\; O \;\text{———}\; CH_2 \end{array} + H_2O,$$

Phenyldehydropentone.

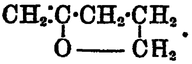
whereas the former, on account of the presence of the methyl group, may yield two internal anhydrides :—



$$\begin{array}{l} CH_3\cdot C{:}CH\cdot CH_2 \\ \quad\;\, O\text{——}CH_2 \end{array}$$

Methyldehydropentone.

and



$$\begin{array}{l} CH_2{:}C\cdot CH_2\cdot CH_2 \\ \quad\;\, O\text{——}CH_2 \end{array}.$$

Methylenetetrahydrofurfuran.

If now, on examination, the anhydride of benzoylpropyl alcohol should be found to be isomeric with benzoyltrimethylene, this fact would obviously be a very strong argument in favour of the trimethylene formula for the latter substance and its derivatives.

In order to decide this point, a quantity of finely-divided benzoyltrimethylenecarboxylic acid was converted into benzoylpropyl alcohol by boiling it with water for four days (see Freer and Perkin, Trans., 1887, **51**, 837), the hot solution filtered from a trace of an oily substance which had formed, rendered slightly alkaline by the addition of potassium carbonate, and the cold turbid liquid extracted several times with pure ether. The ethereal solution after drying over calcium chloride and evaporation, deposited an almost colourless oil which consisted apparently of almost pure benzoylpropyl alcohol. This oil, after removal of the last traces of ether by means of a current of air, gave the following numbers on analysis :—

0·1240 gram substance gave 0·0803 gram H_2O and 0·3348 gram CO_2.

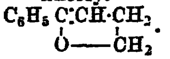
	Theory. $C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$.	Found.
C.........	73·17 per cent.	73·63 per cent.
H.........	7·32 ,,	7·19 ,,
O.........	19·51 ,,	19·18 ,,

When exposed over sulphuric acid in a vacuum, it is slowly but apparently completely converted into its anhydride (Freer and Perkin, *loc. cit.*).

On submitting crude benzoylpropyl alcohol to distillation, water is given off, and a small quantity of a colourless oil distils between 235° and 245°, leaving a considerable residue of high boiling point in the retort.

The fraction 235—245° thus obtained was dried over potassium carbonate, redistilled, and the portion boiling at 240—241° (750 mm.) analysed with the following result :—

0·1425 gram substance gave 0·0930 gram H_2O and 0·4273 gram CO_2.



$$\begin{array}{l}C_6H_5\,C{:}CH\cdot CH_2\\ \quad\;\; O\text{——}CH_2\end{array}$$

	Theory.	Found.
C.........	82·19 per cent.	81·77 per cent.
H.........	6·85 „	7·01 „
O.........	10·95 „	11·22 „

The substance is therefore phenyldehydropentone, the internal anhydride of benzoylpropyl alcohol. Phenyldehydropentone boils practically at the same temperature as benzoyltrimethylene (the latter boils at 239—239·5°, under a pressure of 720 mm.), and it is also very similar to it in appearance, odour, and many other properties. In order to determine whether the two substances were identical or isomeric, the action of hydroxylamine on both, under exactly similar conditions, was investigated.

2 grams of phenyldehydropentone was dissolved in methyl alcohol, mixed with a concentrated aqueous solution of 2 grams of hydroxylamine hydrochloride, a solution of 4 grams of potassium hydrate in methyl alcohol added, and the whole allowed to stand for 15 hours. After distilling off the methyl alcohol, the milky liquid was extracted three times with pure ether, the ethereal solution dried over calcium chloride and evaporated, and in this way about 1 gram of a colourless oil was obtained, which contained no nitrogen, and was most probably unchanged phenyldehydropentone. The alkaline solution, when acidified with hydrochloric acid, deposited an oil; this was extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residual oil, which weighed about 1 gram, heated on a water-bath at 100° for one hour, and analysed with the following result:—

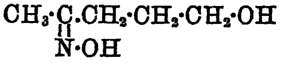
0·1249 gram substance gave 0·0840 gram H_2O and 0·3056 gram CO_2.

0·1823 gram substance gave 12·9 c.c. nitrogen; $t = 18°$; bar. = 7·45 mm.

	Theory. $C_{10}H_{13}NO_2$.	Found.
C.........	67·04 per cent.	66·71 per cent.
H........	7·27 „	7·47 „
N.........	7·82 „	8·08 „

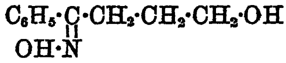
This substance is therefore the oxime of benzoylpropyl alcohol, $C_6H_5\cdot C(NOH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, and the above experiment shows that phenyldehydropentone is itself incapable of forming an oxime, but that in contact with water and hydroxylamine it is slowly converted into the oxime of benzoylpropyl alcohol.

In view of the fact that the oxime of acetopropyl alcohol is entirely converted into its anhydride on heating at 100°, it is very remarkable that the oxime of benzoylpropyl alcohol should remain unchanged at this temperature. This difference may, however, be readily explained, on the assumption that the oxime of acetopropyl alcohol has the β-configuration, that of benzoylpropyl alcohol the α-configuration, thus:—



$CH_3{\cdot}\underset{N\cdot OH}{\overset{}{C}}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$

(β). Oxime of acetopropyl alcohol.



$C_6H_5{\cdot}\underset{OH\cdot N}{\overset{}{C}}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$

(α). Oxime of benzoylpropyl alcohol.

This would be another example in support of Hantzsch's conclusions as to the structure of the ketoximes (*Ber.*, **24**, 31—36), namely, that the mixed aromatic ketoximes all have the α-configuration, whereas the aliphatic ketoximes, on the other hand, are β-oximes.

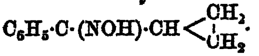
Further experiments are in progress on the oximes of acetopropyl alcohol and benzoylpropyl alcohol, and also on those of the corresponding butyl alcohols; these, it is hoped, will throw more light on this interesting point.

On studying the action of hydroxylamine on benzoyltrimethylene, using the same quantities and working under the same conditions as observed in the case of phenyldehydropentone, very different results from the above were obtained.

The product of the reaction, after distilling off the methyl alcohol, remained perfectly clear, and on acidifying with hydrochloric acid, a copious, oily precipitate was produced which in a short time became quite solid. The precipitate was collected, washed with water, dried on a piece of porous plate, and recrystallised several times from light petroleum and then from water. In this way the oxime of benzoyltrimethylene was obtained in hard, colourless crystals, which melted not very sharply at 90—92°, not at 86—87° as previously stated (Trans., 1885, **47**, 844).

The analysis of these crystals gave the following numbers:—

0·1745 gram substance gave 13·5 c.c. nitrogen; $t = 16°$; bar. = 745 mm.



$C_6H_5{\cdot}C{\cdot}(NOH){\cdot}CH{<}\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}.$

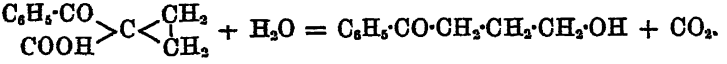
	Theory. $C_6H_5{\cdot}C{\cdot}(NOH){\cdot}CH{<}\begin{matrix}CH_2\\ CH_2\end{matrix}$.	Found.
N.......	8·69 per cent.	8·84 per cent.

Considerable difficulty was experienced in obtaining this substance in a pure condition; it appeared to be a mixture of two compounds, and it is therefore possible that the oxime of benzoyltrimethylene exists in two modifications.

In view of the results obtained in these experiments, there can now be no doubt that benzoyltrimethylene and phenyldehydropentone are totally different compounds.

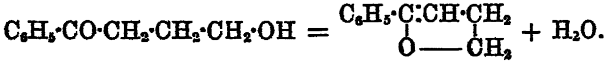
Phenyl Tetramethylene Glycol, $C_6H_5\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, *and Phenyl Tetramethylene Dibromide*, $C_6H_5\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2Br$.

In a previous investigation by P. C. Freer and one of us (Trans., 1887, 51, 837), the action of water on benzoyltrimethylenecarboxylic acid at 100—110° was carefully studied, as it was thought that in this way benzoylpropyl alcohol might be obtained, thus:—



$$\begin{matrix}C_6H_5\cdot CO\\ COOH\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + H_2O = C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + CO_2.$$

This decomposition would be analogous to the formation of acetopropyl alcohol from acetyltrimethylenecarboxylic acid by boiling it with water (Trans., 1887, 51, 829). Although present in the aqueous solution obtained, it was not, at that time, found possible to isolate this ketone alcohol, owing to the fact that it decomposes at ordinary temperatures into water and its anhydride, methyldehydropentone, thus:—



$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH = \begin{array}{l}C_6H_5\cdot C{:}CH\cdot CH_2\\ \qquad\;\, | \qquad\quad |\\ \qquad\;\, O \text{———} CH_2\end{array} + H_2O.$$

(For later experiments, see p. 887.)

In a subsequent investigation by Dr. Schloesser and one of us, these experiments were repeated, and on treating the aqueous solution of benzoylpropyl alcohol with sodium amalgam we obtained phenyl tetramethylene glycol, thus:—

$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + H_2 = C_6H_5\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

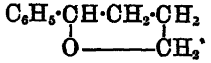
and this, being much more stable than the ketone alcohol, could be isolated without difficulty in the usual way.

Pure benzoyltrimethylenecarboxylic acid was dissolved in ammonia, reprecipitated by dilute hydrochloric acid, and the finely-divided acid thus obtained boiled with a considerable quantity of water for about three days until the evolution of carbonic anhydride had entirely ceased. The warm aqueous solution was filtered from a very small quantity of phenyldehydropentone, which is always formed, and then treated in a flat dish with four times the calculated quantity of sodium amalgam (2½ per cent.) in small quantities at a time, carbonic anhydride being passed through the liquid during the reduction. The product was saturated with potassium carbonate, extracted several times with ether, the ethereal solution dried over calcium chloride, concentrated on a water-bath, and then allowed to evaporate spontaneously in a glass dish. In this way, the new glycol was obtained in hard, crystalline crusts, which, after recrystallisation from ether, gave on analysis the following numbers:—

0·1736 gram substance gave 0·1326 gram H_2O and 0·4594 gram CO_2.

	Theory. $C_{10}H_{14}O_2$.	Found.
C	72·17 per cent.	72·21 per cent.
H	8·44 „	8·48 „
O	19·28 „	19·23 „

Phenyl tetramethylene glycol melts at 75°. It is readily soluble in alcohol, ether, and hot water, but only sparingly in cold water. When heated at a high temperature, it is decomposed, water is split off, and a thick, colourless oil distils which is probably phenyl tetramethylene oxide,



$$\begin{array}{l}C_6H_5\cdot \underset{|}{C}H\cdot CH_2\cdot \underset{|}{C}H_2\\ O\text{———}CH_2.\end{array}$$

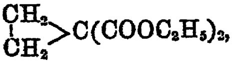
Phenyl Tetramethylene Dibromide.—Phenyl tetramethylene glycol is readily acted on by fuming hydrobromic acid at 100° with formation of a thick, oily substance which appears to be a mixture of the monobromhydrin of phenyl tetramethylene glycol with phenyl tetramethylene dibromide, but all attempts to isolate the pure dibromide from this mixture were unsuccessful. Ultimately the following method of preparing this substance, which is almost identical with that employed by Kipping and Perkin in the preparation of phenyl pentamethylene dibromide (Trans., 1890, **57**, 314), and gives a good yield of the almost pure product, was adopted. The pure glycol dissolved in chloroform is treated with 1½ times the calculated quantity of phosphorus pentabromide in small quantities at a time at ordinary temperatures until all action has ceased. The solution is then decanted from any undecomposed pentabromide, washed well with water, dried over calcium chloride, evaporated on a water-bath, and the last traces of chloroform removed by exposure over paraffin under reduced pressure. In this way, a thick, almost colourless oil is obtained which on analysis gave the following numbers:—

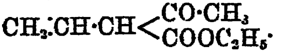
0·2010 gram substance, heated at 180° with nitric acid and nitrate of silver, gave 0·2560 gram AgBr.

	Theory. $C_{10}H_{12}Br_2$.	Found.
Br.......	54·80 per cent.	54·18 per cent.

Phenyl tetramethylene dibromide is a very thick, almost colourless oil which on standing in the air gradually darkens.

Experiments on the Behaviour of Ethyl Acetyltrimethylenecarboxylate towards Isoamyl Iodide in the presence of Sodium Ethylate.

In studying the properties of ethyl trimethylenedicarboxylate,  $\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>C(COOC_2H_5)_2$, it was found to behave in all respects as a disubstituted ethyl malonate derivative: that is, it was incapable of forming a sodium compound when treated with sodium ethylate; hence its constitution could not be represented by the formula $CH_2{:}CH{\cdot}CH(COOC_2H_5)_2$ (Trans., 1885, **47**, 821, and 1887, **51**, 849).

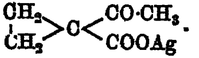
Now, if ethyl trimethylenedicarboxylate and ethyl acetyltrimethylenecarboxylate are similarly constituted, it follows that the latter shou'd also be incapable of forming a sodium compound, a hypothesis which was fully borne out by experiment. Hence ethyl acetyltrimethylenecarboxylate cannot be represented by the formula  $CH_2{:}CH{\cdot}CH{<}\begin{array}{l}CO{\cdot}CH_3\\ COOC_2H_5\end{array}$.

The experiment was conducted as follows:—

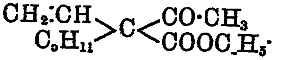
28 grams of pure ethyl acetyltrimethylenecarboxylate was mixed with sodium ethylate containing 4·2 grams of sodium, 64 grams of isoamyl iodide added, and the mixture heated for five hours on a water-bath in a flask connected with a reflux apparatus. After distilling off the alcohol as completely as possible, the residue was diluted with water, extracted several times with ether, the ethereal solution washed, dried over calcium chloride, and evaporated. A very small quantity of an ethereal oil was thus obtained; this, on fractionation, distilled principally between 195° and 210°, and consisted of slightly impure ethyl acetyltrimethylenecarboxylate; there was scarcely any residue boiling above 210° left in the retort.

The aqueous liquors were evaporated to expel alcohol, acidified with dilute sulphuric acid, and repeatedly extracted with ether. The ethereal solution was dried over calcium chloride and evaporated, when about 19 grams of an almost colourless oil remained, which, on examination, was found to consist of acetyltrimethylenecarboxylic acid. The crude acid was converted into the characteristic silver salt, and this, after recrystallisation, analysed with the following result:—

0·2367 gram substance gave on ignition 0·1083 gram silver.



	Theory. $\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>C{<}\begin{array}{l}CO{\cdot}CH_3\\ COOAg\end{array}$.	Found.
Ag........	45·89 per cent.	45·76 per cent.

This experiment proves that ethyl acetyltrimethylenecarboxylate is incapable of forming a sodium compound which, when treated with isoamyl iodide, would yield a higher homologue, and, therefore, the constitution of this ethyl salt cannot be represented by the formula $\mathrm{CH_2{:}CH{\cdot}CH}<\begin{array}{l}\mathrm{CO{\cdot}CH_3}\\ \mathrm{COOC_2H_5}\end{array}$, as a substance of that constitution would, by such treatment, have been converted into ethyl isoamylvinylacetoacetate,  $\begin{array}{l}\mathrm{CH_2{:}CH}\\ \mathrm{C_5H_{11}}\end{array}>\mathrm{C}<\begin{array}{l}\mathrm{CO{\cdot}CH_3}\\ \mathrm{COOC_2H_5}\end{array}$.

Action of Ethylene Bromide on the Sodium Compound of Ethyl Ethylacetoacetate.

In the preceding section of this paper, it was shown that attempts to introduce the alkyl radical isoamyl into the molecule of ethyl acetyltrimethylenecarboxylate were unsuccessful: the reason assigned being that, as a disubstituted ethyl acetoacetate derivative, this ethereal salt was incapable of forming a sodium compound which, when treated with an alkyl iodide, would yield higher homologues.

If this deduction be true, it follows that ethyl ethylacetoacetate, $CH_3{\cdot}CO{\cdot}CH(C_2H_5){\cdot}COOC_2H_5$, when treated with sodium and ethylene bromide, should also be incapable of yielding an ethyl substituted ethyl acetyltrimethylenecarboxylate. The following experiment was instituted with the object of testing this hypothesis:—

A mixture of 175 grams of ethyl ethylacetoacetate, 110 grams of ethylene bromide, and 26 grams of sodium (in the form of sodium ethylate) was heated for six hours on a water-bath, the alcohol then distilled off, water added, and the product extracted three times with ether. The ethereal solution was evaporated, and the oily residue submitted to distillation in a rapid current of steam, when it was found that almost the whole distilled over, leaving only a very small quantity of an oily residue in the retort. The distillate was extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residual oil purified by fractional distillation. It was thus roughly separated into two fractions 120—200° (70 grams) and 200—240° (about 20 grams). The first portion, on careful repeated refractionation from a Würtz' flask provided with a long neck, yielded a large quantity of a colourless oil boiling constantly at 120°, and which, on examination, was found to consist of pure ethyl butyrate.

I. 0·1534 gram substance gave 0·3470 gram CO_2 and 0·1447 gram H_2O.

II. 0·1309 gram substance gave 0·2955 gram CO_2 and 0·1239 gram H_2O.

	Theory. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_2H_5$.	Found. I.	 II.
C	62·08 per cent.	61·69	61·57 per cent.
H	10·34 „	10·48	10·28 „
O	27·58 „	27·83	28·15 „

This ethereal salt was hydrolysed by boiling with potassium hydrate solution, and the acid obtained by acidifying the solution with hydrochloric acid and extraction with ether boiled constantly at 162—163°, and showed all the properties of normal butyric acid. The formation of ethyl butyrate in this reaction must be due to the partial hydrolysis of the ethyl ethylacetoacetate, brought about probably by the prolonged boiling of its sodium compound,

$$CH_3{\cdot}CO{\cdot}CH(C_2H_5){\cdot}COOC_2H_5 + H_2O = CH_3{\cdot}COOH + CH_2(C_2H_5){\cdot}COOC_2H_5.$$

The higher boiling fraction, obtained as described above, was submitted to most careful fractionation, but nothing definite could be isolated. The whole was therefore hydrolysed, and thus converted into a neutral substance (which was not examined), and a very small quantity of an oily acid.

As this acid might possibly have been an ethyl derivative of acetyltrimethylenecarboxylic acid, a number of experiments were instituted with the object of proving its identity. As, however, the substance was not attacked by fuming hydrobromic acid with formation of a substituted acetopropyl bromide, nor decomposed by boiling with water yielding a substituted acetopropyl alcohol, there can be no doubt that an acid constituted analogously to acetyltrimethylenecarboxylic acid was not present.

LXXIX.—*The Gravivolumeter, an Instrument by means of which the Observed Volume of a Single Gas gives directly the Weight of the Gas.*

By Francis R. Japp, F.R.S.

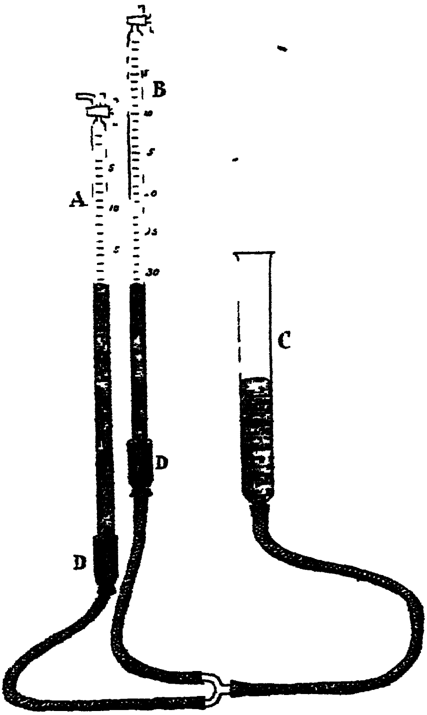
An apparatus for effecting this object has been described by Lunge (*Ber.*, **23**, 448; see also *Ber.*, **24**, 735); but his method labours under the disadvantage of requiring for each gas a separate apparatus with a special graduation. Thus Lunge's apparatus for measuring nitrogen is a "gas volumeter," with divisions of 0·798 c.c. (further subdivided into tenths), each of which divisions will contain a milligram of nitrogen under standard conditions. The reduction to standard state is effected mechanically by means of the "regulator" attached to his gas volumeter.

Another method employed by Lunge (*J. Soc. Chem. Ind.*, 9, 23), available in cases in which the gas evolved from a solid or liquid substance has to be determined, consists in weighing out such a quantity of substance that the number of cubic centimetres of "standard-dry" gas evolved will represent the percentage by weight of this gas contained in the original substance. The method is available only in this particular class of cases, and gives only the percentage weight, not the absolute weight, of the gas.

I wish to point out how, by slightly modifying Lunge's gas volumeter, an apparatus may be constructed by means of which, with an ordinary graduation in cubic centimetres, any required single gas may, without observation of temperature or pressure and without calculation, be measured under such conditions that each cubic centimetre represents a milligram of the gas. For this purpose it is necessary that the "regulator" of Lunge's instrument, which is wider above than below, and is graduated only between the divisions 100 and 130 c.c., should be replaced by an ordinary 50 c.c. gas burette which can be read throughout. The method of reduction by means of this regulator differs from that employed by Lunge.

The apparatus is represented in the annexed drawing (p. 896). It consists of two gas burettes, of 50 c.c. capacity each, both furnished with obliquely bored taps. One of these burettes, A, which has a three-way tap, is the gas measuring tube; the other, B, which need only have a single tap, performs, as already mentioned, the function of the regulator in Lunge's gas volumeter, and may be termed the "regulator tube." As in Lunge's instrument, both tubes are moistened internally with a drop of water, in order that the gases they contain may be saturated with aqueous vapour, and both are connected, by means of stout, flexible tubing and a T-piece, with the *same* movable reservoir of mercury, C. And since, in certain determinations, the level of the mercury reservoir is considerably below the lower end o the two burettes, and an inward leakage of air might thus occur at the junctions of the burettes with the india-rubber tubing, these junctions are surrounded with pieces of wider india-rubber tubing, D, D, tied round the bottom and open at the top, and filled with water, so as to form a water-joint.

The 25 c.c. division of the regulator tube is taken as the starting point in calculating what may be termed the "gravivolumetric values" of the different gases to be measured. Thus in the case of nitrogen it is necessary to calculate to what volume 25 c c. of standard-dry nitrogen must be brought in order that 1 c.c may correspond with 1 milligram of the gas; that is to say, 25 c.c. of standard-dry nitrogen weigh 0·001256 × 25 = 0·0314 gram; and, therefore, these 31·4 miligrams must be brought to the volume of 31·4 c.c. The division 31·4 on the *regulator* tube is marked N$_2$. Corresponding



points are in like manner determined for the various other gases which it is desired to measure, and these points are marked O$_2$, CO$_2$, &c., as the case may be, on the regulator tube. Finally, the thermometer and barometer are read (a process only necessary once for all in setting the regulator), the volume which 25 c.c. of standard-dry air would occupy if measured moist at the observed temperature and pressure is calculated, and this calculated volume of air is admitted at atmospheric temperature and pressure into the regulator tube and the tap closed. The instrument is now ready for use.

Suppose it is desired to ascertain the weight of a quantity of nitrogen contained in the measuring tube. The mercury reservoir is raised or lowered until the mercury in the regulator tube stands at the nitrogen mark, 31·4, at the same time adjusting the regulator tube itself by raising or lowering it bodily, so that the mercury level in the measuring tube and the regulator tube may be the same. *Under these circumstances each cubic centimetre of gas in the measuring tube represents* 1 *milligram of nitrogen.* For since in the regulator tube 25 c.c. of standard-dry air have been made to occupy the volume of 31·4 c.c., and since the gases in the two tubes are under the same conditions as regards temperature, pressure, and saturation with aqueous vapour, therefore, in the measuring tube, every 25 c.c. of standard-dry nitrogen have also been made to occupy the volume of 31·4 c.c. But 25 c.c. of standard-dry nitrogen weigh, as we have seen, 31·4 milligrams: so that the problem is solved, and the cubic centimetres and tenths of cubic centimetres give directly the weight of the gas in milligrams and tenths of milligrams.

The various other single (*i.e.*, unmixed) gases may be weighed in like manner by bringing the mercury in the regulator tube to the "gravivolumetric mark" of the gas in question, and adjusting the levels as before. An exception would be made in the case of hydrogen, which would be brought to such a volume that the cubic centimetre would contain a *tenth* of a miligram.

Mixtures of gases may also be weighed, provided that the density of the mixture is known.

Lastly, if the mercury in the regulator tube be brought to the mark 25 and the levels adjusted, a gas or mixture of gases in the measuring tube will have the volume which it would occupy in the standard-dry state. In this form the instrument is merely a gas volumeter, as described by Lunge, and may be used for ordinary gas analysis.

It remains to describe the experiments made with the view of ascertaining the degree of accuracy of which the apparatus is capable.

The capacity of the burettes employed had been measured for every 10 c.c. by the maker in the process of graduating them; but I further calibrated them, before use, by filling the tubes above the mercury with water, displacing the water upwards through the taps by mercury, and weighing the water displaced from every 4 c.c. of the tubes. The *differences* of capacity—50—46 c.c., 46—42 c.c., &c.—were found to be practically accurate as far as division 2; but in both burettes the difference 2—0 c.c. was found to represent a capacity of 2·2 c.c. instead of 2 c.c., the result being that from division 2 to division 50 the actual capacity of the burettes was everywhere 0·2 c.c. greater than the nominal capacity.* This correction of 0·2 was, therefore, *added* to the readings of the measuring tube, and the same amount was *deducted* in filling the regulator and in fixing the gravivolumetric marks. The formulæ indicating the latter were not engraved on the tube, as recommended in the foregoing; instead, a thin india-rubber band, slipped round the regulator tube, was placed at the division just below the gravivolumetric mark, and served to guide the eye.

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* The assumption that the maker had measured the capacity of the *inverted* burette with mercury would only partially account for this error.

The measuring tube and regulator tube were held by a double clamp, the arms of which could be moved horizontally, so as to admit of bringing the tubes close together when necessary.* The two tubes were so arranged that, after adjusting the levels and ascertaining that the mercury in the regulator tube was at the gravivolumetric mark, it was possible to read both levels without moving the position of the eye. The object of this was that any possible error of parallax might occur equally and in the same direction in both tubes, in which case the two errors would tend to neutralise one another in the final result.† The mercury reservoir was held by a clamp attached to a separate stand, so that in the case of extreme differences of pressure the entire stand could be placed on a different level from the rest of the apparatus.

As it was obviously unnecessary, in the trial measurements, that the apparatus should contain the actual gases under consideration, the following plan was adopted:—

After filling the regulator in the manner already described, the tap of the measuring tube was opened, and any desired volume of air was admitted by lowering or raising the mercury reservoir. The point where the mercury stood in the measuring tube was noted, and the tap was then closed; barometer and thermometer were also read. The measuring tube thus contained a known volume of moist air, which had been measured at known (atmospheric) temperature and pressure. This quantity of air was then gravivolumetrically measured (1) as methane, (2) as nitrogen, (3) as air itself, and (4) as carbon dioxide, the first and last being selected as giving the extremes of density with which it would in practice be necessary to deal, excepting the case of hydrogen before referred to. The weight of the air was then, from the original data of volume, temperature, and pressure, calculated on these same four assumptions, and the calculated weights were compared with those obtained by the gravivolumetric method.

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* I have not had an opportunity of reading a description of the double clamp (*Gabelklammer*) used by Lunge. His method of adjusting the levels by fixing the measuring tube and the mercury reservoir in the same double clamp is not applicable to the gravivolumeter on account of the differences of pressure which it is frequently necessary to employ with this instrument.

† Suppose the eye in reading to be too high, the mercury in the regulator would stand *below* the gravivolumetric mark, and the gas in the measuring tube would consequently be expanded beyond its proper volume. But owing to the eye being too high, this too great volume in the measuring tube would be read off as smaller than it actually is. In the case of equal volumes of gas in regulator and measuring tube, there would thus be a total correction of the error committed (since the two tubes are of equal bore), and in every case a diminution.

Four series of experiments were made, the results of which are here tabulated. In the first series, the air was not gravivolumetrically measured as air itself, the idea of making this measurement not having occurred to me at that time. No observation has been rejected.

The gravivolumetric values are:—Methane, 17·9; nitrogen, 31·4; air, 32·35; carbon dioxide, 49·3. Reference has already been made to the correction introduced.

The first column of figures contains the gravivolumetric measurements in "milligram cubic centimetres"; the second the calculated weights in milligrams.

Experiment I.

	v.	*t.*	Bar.
Air (moist) in measuring tube	16·25 c.c.	14·5°	772 mm.

	Volume in mgr.-c.c.	Calculated weight in mgr.
As CH_4......	11·10	11·07
,, N_2........	19·40	19·38
,, CO_2......	30·40	30·45

Experiment II.

	v.	*t.*	Bar.
Air (moist) in measuring tube	18·5 c.c.	14·5°	768 mm.

	Volume in mgr.-c.c.	Calculated weight in mgr.
As CH_4......	12·55	12·54
,, N_2........	21·95	21·95
,, air	22·60	22·60
,, CO_2......	34·45	34·49

Experiment III.

	v.	*t.*	Bar.
Air (moist) in measuring tube	21·3 c.c.	15·5°	758 mm.

	Volume in mgr.-c.c.	Calculated weight in mgr.
As CH_4......	14·15	14·18
,, N_2........	24·85	24·82
,, air	25·60	25·55
,, CO_2......	39·05	39·00

Experiment IV.

	v.	t.	Bar.
Air (moist) in measuring tube	25·0 c.c.	15°	764 mm.

	Volume in mgr.-c.c.	Calculated weight in mgr.
As CH_4......	16·80	16·82
„ N_2........	29·45	29·43
„ air	30·35	30·30
„ CO_2......	46·30	46·25

Assuming the graduation of a gravivolumeter to be correct, or the defects of graduation to be eliminated by calibration, the sources of error in such an instrument are, broadly speaking, four in number, and are to be found in imperfections (1) in filling the regulator, (2) in adjusting the levels, (3) in reading the regulator, and (4) in reading the measuring tube. The first of these operations, that of filling the regulator, is performed once for all with very great care, and may, for all practical purposes, be disregarded as a source of error. Again, in adjusting the levels, the two tubes can be brought, by means of the double clamp, within such a short distance of one another that the adjustment is also practically accurate. The sources of error lie in the two last operations. The burettes are divided into tenths of cubic centimetres, and can be read with the eye alone accurately to 1/20 c.c. Calculating this error on 25 c.c. as the average volume of gas contained in the regulator tube and measuring tube respectively, we have 1/(20 × 25) = 1/500 as the error for each tube. But as the error in the regulator repeats itself in exact proportion in the altered volume of gas in the measuring tube, we must add the error of the regulator to the independent error of the measuring tube, in order to ascertain the maximum error, which would thus be 1/250; and this, calculated as assumed, upon 25 c.c. of gas, would be equal to an error of reading of 0·1 c.c. in the final result. An inspection of the foregoing experimental results, however, discloses the fact that the maximum error is only half this amount, or 0·05 c.c.; and this I attribute to the fact that, owing to the method of reading employed, the errors of reading in the regulator and measuring tube are not, as assumed in the foregoing calculation, independent, but tend to neutralise one another (*vide supra*).

This error of 0·05 c.c. is, however, the error of reading of any gas burette which is read with the eye alone; and the gravivolumeter may, therefore, claim to possess the same degree of accuracy as instruments of this class generally.

The gravivolumeter is designed to fulfil a variety of purposes for which Lunge employs a number of different gas volumeters, and from the foregoing I anticipate that it will fulfil these purposes equally well. In addition, it is no small advantage of the apparatus that, unlike Lunge's specially graduated gas volumeters, it makes no claim upon the skill of the instrument maker beyond that of carrying out the ordinary graduation in cubic centimetres with which he is familiar.

In analytical processes in which the weight of a gas evolved from a weighed quantity of substance has to be determined, the instrument ought to be of service. It is sufficiently accurate for technical purposes, and even for some scientific purposes, such as the absolute determination of nitrogen in organic substances, and the determination of the weight of displaced air in V. Meyer's vapour density method, purposes for which Lunge has employed his gas volumeter.

My preliminary note on the subject of the gravivolumeter (Proc., 1891, 68) has been criticised by Professor Lunge (*Ber.*, **24**, 1656). One or two points of this criticism appear to me to rest on a misunderstanding.

Professor Lunge begins by quoting my statement that the gravivolumeter is, with a slight modification, identical with his gas volumeter, and adds that it is "absolutely identical." He then goes on to say that, by altering the form of the regulator, I have so diminished the accuracy of the instrument as to render it useless for many purposes. I fear I must leave Professor Lunge to reconcile these two statements. I will return later, however, to this question of the supposed diminished accuracy.

Professor Lunge denies that there is anything new in the principle of reading off volumes directly as weights in an apparatus divided into cubic centimetres, because, he says, he has effected this by the device of employing determinate weights of substance. (This refers to the case to which I have already alluded in the beginning of this paper, in which the gas evolved from a solid or liquid substance has to be determined.) Here Professor Lunge neglects to distinguish between absolute weight and percentage weight. My method gives the absolute weight of the gas; his method gives only the percentage weight referred to the weight of substance taken, and can, under no circumstances, give directly the absolute weight.

Professor Lunge admits that the principle of so regulating the pressure in the case of each gas that a cubic centimetre represents a milligram is new, and this is all that I ever claimed as such. The name "gravivolumeter," however, appears to give him offence, for he says: "I am unable to see why Japp should give my instrument a new name, merely because he takes the readings in a slightly different way." I may say that the name "gravivolumeter" was intended to express, amongst other things, the family relationship of the instrument to Professor Lunge's "volumeter," and was thus an acknowledgment of obligation; as, indeed, the acknowledgments of obligation throughout my entire note could hardly have been more profuse. The name may or may not find acceptance; but I should apply it to any form of gas volumeter which reduces volume directly to weight; thus I should term Professor Lunge's apparatus with divisions of 0·798 c.c. a nitrogen gravivolumeter, while mine is a universal gas gravivolumeter.

I have reserved until the last Professor Lunge's strictures on the supposed diminished accuracy of the instrument. Referring to the system of reduction of volume employed by me, he says: "It involves that the reduction tube, instead of having the form which I gave to it—expanded in the upper part and capable of being read with an accuracy of 1/20 c.c. between the degrees of 100—130 c.c.—is of cylindrical form and of only 50 c.c. capacity; and further, that the normal volume is, not 100 c.c., but only 25 c.c., of air. In this way the accuracy of the observations is *a priori* reduced to $\frac{1}{4}$, and, on account of the inconvenient form of the tube, probably even to $\frac{1}{8}$, of that attainable with my form of tube. In fact, Japp himself anticipates only* a degree of accuracy sufficient for technical purposes, whilst with my system a degree of accuracy to $1/(100 \times 20) = 1/2000$, quite sufficient for most scientific purposes, can be attained without the slightest difficulty."

I entirely fail to follow the reasoning with regard to the inconvenient form of the tube, as it is quite evident that two cylindrical burettes can be brought closer together, and the levels, therefore, more accurately adjusted, than if one of the tubes bulges above the graduated portion, like Professor Lunge's regulator.

But the chief point to which I wish to call attention in Professor Lunge's argumentation is the way in which he tacitly assumes throughout that the only source of error in the instrument lies in a faulty adjustment of the regulator, and that because his regulator can be adjusted four times as accurately as mine, therefore the indications of his instrument are four times as accurate. I have already discussed the way in which the errors of the regulator tube and measuring tube might be expected to combine, and if it be borne in mind that in Professor Lunge's instrument, as in my own, the final reading is made with a 50 c.c. burette, which cannot be read, with certainty, to nearer than 1/20 c.c., the advantages of the superior accuracy of adjustment of his regulator will appear problematical, and his estimate of the capabilities of his instrument unduly favourable. The foregoing calculation, $1/(100 \times 20) = 1/2000$, gives the error of his regulator; the error of the measuring tube, calculated on the basis of 25 c.c. as the average amount of gas measured, would be $1/(25 \times 20) = 1/500$, or four times that amount. But in Professor Lunge's discussion of the question, the greater of these two errors is entirely ignored. It is a commonplace of physical measurement that there is no advantage in making one of the interdependent parts of a determination exceedingly accurate, if the result is vitiated by a much greater error in another part.

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* Professor Lunge unintentionally exaggerates the modesty of my anticipations. The words in my note which he renders by *nur* (only) were "at all events."

I do not think that Professor Lunge can get rid of the error of 1 20 c.c. in reading his measuring tube; and this, as I have experimentally shown, is the maximum error of my instrument.

I venture to oppose my experimental proof of what the gravivolumeter can do to Professor Lunge's theoretical prognostications of what it cannot do.

University of Aberdeen.

LXXX.—*On the Vapour Pressures and Molecular Volumes of Acetic Acid.*

By Sidney Young, D.Sc., Professor of Chemistry, University College, Bristol.

The thermal properties of acetic acid have been studied by many observers, among others, Playfair and Wanklyn, Bineau, Cahours, Regnault, Naumann, and Horstmann. In 1886, the vapour pressures, specific volumes, and vapour densities of this substance were determined by Dr. Ramsay and myself (Trans., 1886, **49**, 790) up to 280°, but we were unable at the time to reach higher temperatures. The addition of dibenzyl ketone to the list of pure substances suitable for heating agents has, however, enabled me to extend the observations to the critical point of acetic acid.

The same specimen of acid was employed as in the previous investigation; it was carefully fractionated to remove water, and the boiling point was determined on various occasions with the following results:—

Pressure.	Boiling point.	Corrected to 760 mm.
753·5	118·1	118·35
756·6	118·2	118·35
758·7	118·27	118·32
756·7	118·22	118·36
	Mean ..	118·35

The vapour pressures and specific volumes were determined in a modified Andrews' apparatus similar to that previously employed, and the corrections of the pressure were the same as before.

In filling the tube, great care was taken to avoid the presence of moisture; the acid was freshly distilled each time, and the distillate was collected directly in the little glass vessel from which the tube was filled. The glass vessel was also placed, during the distillation, in a drying chamber containing dishes of sulphuric acid and of phosphorus pentoxide, the delivery tube from the distillation bulb passing through a perforated sheet of india-rubber into the chamber. In this way the acid was prevented from coming in contact with moist air.

Some readings of pressure and volume were taken at temperatures below 280°, and, as two tubes burst during the investigation, there are three separate series of determinations of vapour pressures and two of specific volumes.

Vapour Pressure.

Series I.

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
240°	12509	12492	270°	20696	20646
	12495			20653	
	12484			20624	
	12478			20610	
250°	14876	14856	280·25°	24251	24224
	14859			24197	
	14851				
	14836				
260°	17584	17567			
	17593				
	17549				
	17542				

Series II.

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
150°	1877 1875 1875 1875	1875	230°	10433 10398 10395 10400	10406
160°	2414 2408 2407 2407	2409	240°	12516 12507 12506 12517	12511
170°	3062 3058 3058 3053	3058	250°	14903 14886 14862 14855	14876
180	3838 3836 3829 3827	3833	260°	17632 17595 17563 17572	17590
190	4746 4738 4735 4729	4737	270°	20721 20653 20629 20621	20656
200°	5849 5846 5843 5832	5843	280 7°	24449 24367 24346 24366	24382
210°	7150 7135 7140 7130	7139	290°	27666 27651 27662 27682	27665
220°	8656 8646 8642 8640	8646	300°	32114 32080	32097

Series III.

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
190°	4730 4729 4728 4728	4729	210°	7120 7109 7108 7108	7111
200°	5829 5823 5820 5820	5823	220°	8636 8622 8630 8630	8630

Section III—continued.

Temp.	Pressure	Mean.	Temp.	Pressure	Mean
230°	10398 10390 10413 10388	10397	310°	36928 36948 36952	36943
290°	27589 27564	27576	320°	42563 42542	42553
300°	32001 31974 31906 32066	31987	321·65 (critical temp.)	43404	43404

The vapour pressure agrees fairly well with those observed by Ramsay and myself, but are rather lower at high temperatures. I have, therefore, calculated the constants for Biot's formula ($\log p = a + b\alpha^t + c\beta^t$) for a range of temperature from 120° to 320°, the old

Table of Vapour Pressures.

Temperature.	Mean pressure observed.	Calculated from new constants.	Calculated from old constants.
120°	—	804	794
130	—	1083	1068
140	—	1431	1414
150	1875	1863	1847
160	2409	2392	2382
170	3058	3034	3035
180	3833	3809	3826
190	4733	4735	4775
200	5833	5836	5905
210	7125	7134	7238
220	8638	8655	8800
230	10402	10426	10619
240	12501	12475	12724
250	14866	14832	15144
260	17579	17527	17913
270	20651	20590	21063
280	24123*	24055	24629
290	27621	27951	—
300	32043	32312	—
310	36943	37168	—
320	42553	42550	—

* Calculated from observations at 280·25° and 280·7°.

values at lower temperatures being taken as correct. The constants are:

$$a = 6{\cdot}29974;$$

$$\log b = 0{\cdot}5226921; \qquad \log c = \bar{2}{\cdot}7963908;$$

$$\log \alpha = \bar{1}{\cdot}99850102; \qquad \log \beta = \bar{1}{\cdot}98695760;$$

b and c are both negative; $t = t^\circ$ C. — 120.

In the preceding table, the pressures calculated from these constants are compared with those found experimentally and with the values calculated by Ramsay and myself from the old constants for Biot's formula:—

Volumes of a Gram and Molecular Volumes of Liquid.

In the following table, I have given the observed volumes of a gram of liquid and the molecular volumes calculated from the mean values, also the molecular volumes read from a curve, and those previously observed by Dr. Ramsay and myself:—

Temperature.	Volume of a gram.			Molecular volumes.		
	Series I.	Series II.	Mean.	Mean from observed values.	From curve.	R. & Y. observed.
140·0°	1·100	—	1·100	65·84	65·84	65·69
150·0	1·116	—	1·116	66·83	66·79	66·68
160·0	1·134	—	1·134	67·90	67·80	67·76
170·0	1·151	—	1·151	68·89	68·85	68·66
180·0	1·169	—	1·169	69·96	69·97	69·84
190·0	1·188	1·188	1·188	71·11	71·15	71·29
200·0	1·210	1·210	1·210	72·43	72·43	72·60
210·0	1·233	1·232	1·232	73·79	73·82	74·04
220·0	1·260	1·258	1·259	75·36	75·38	75·56
230·0	1·287	1·291	1·289	77·18	77·10	77·33
240·0	1·320	—	1·320	79·03	79·06	79·21
250·0	1·359	—	1·359	81·34	81·29	81·90
260·0	1·401	—	1·401	83·84	83·89	84·16
270·0	1·450	—	1·450	86·79	86·75	87·21
280·7	1·516	—	1·516	90·72 (280°)	90·30	90·77
290·0	1·578	1·577	1·578	94·44	94·50	—
300·0	—	1·679	1·679	100·5	100·6	—
310·0	—	1·844	1·844	110·4	110·4	—
320·0	—	2·167	2·167	129·7	129·7	—
321·5	—	2·375	2·375	142·2	142·0	—
321·55°	—	2·41	2·41	144·0	144·0	—
321·65	—	2·46	2·46	147·0	147·0	(Critical volume)

As the two series of determinations were made with different tubes, the agreement is very satisfactory. The new results agree also fairly well with the old ones.

Critical Constants.

The following observations were made near the critical point:—

At 321·5°. the meniscus could be made to disappear by diminishing the volume rapidly; it was, however, quite distinct, though flat, when the volume remained constant.

At 321·55°, the meniscus was indistinct, but became clearly defined on increasing the volume slightly.

At 321·65°, the substance was apparently at its critical point; a momentary separation of liquid and vapour could be produced by increasing the volume slightly but rapidly.

At 321·8°, a dense mist and striæ were formed on increasing the volume, and it was just possible to obtain a faint line of separation of liquid and vapour by a rapid and more considerable increase of volume.

The acetic acid was assumed to occupy its critical volume when a very slight but rapid expansion gave a momentary line of demarcation of liquid and vapour almost exactly at the top of the tube.

The critical temperature 321·65° is almost identical with that observed by Pawlewski, 321·5° (*Ber.*, **16**, 2633). The critical pressure is 43400 mm., the critical volume of a gram 2·46 c.c., and the critical molecular volume 147 c.c.

Volumes of a Gram and Molecular Volumes of Saturated Vapour.

Some determinations were made by the new method (Trans., 1891, **59**, 37), but, unfortunately, the tube burst at 280°. The agreement with the previous results by Ramsay and myself is good from 220° to 280°, as will be seen from the table.

A determination was also made at 310° in the modified Andrews' apparatus by observing the volume of liquid when all the vapour was condensed, and afterwards with different volumes of vapour above the liquid.

From four readings of the volume of liquid, three calculations of the ratio of the specific volume of saturated vapour to that of liquid could be made; they gave the values 3·16, 3·21, 3·08—mean 3·15. From this, the volume of a gram and molecular volume of saturated vapour were calculated. The molecular critical volume, as already stated, is 147 c.c. The logarithms of the molecular volumes were mapped against the temperature and a curve constructed; the smoothed logarithms were read from the curve, and the molecular volumes corresponding to them are given in the table together with the observed values.

Temperature	Observed volumes of a gram.			Molecular volumes.	
	New method	Old method.	R. & Y.	Observed.	From curve.
220·0°	32·9	—	33·32	1971	1982
230·0	27·7	—	27·72	1657	1652
240·0	23·2	—	23·12	1386	1384
250·0	19·3	—	19·32	1157	1160
260·0	16·1	—	16·17	966	971
270·0	13·6	—	13·51	813	813
280·0	11·4	—	11·21	682	678
290·0	—	—	—	—	558
300·0	—	—	—	—	450
310·0	—	5·81	—	348	349
320·0	—	—	—	—	231
321·65°	—	2·46	—	147	147

Special interest attaches to the determination of the densities of the saturated vapour of acetic acid, because it is believed that the abnormally high values at low temperatures are due to the existence of complex molecules. I have, therefore, calculated the vapour densities corresponding to the above molecular volumes and also the ratios of the actual vapour densities to the theoretical density for the formula $C_2H_4O_2$.

The results are given in the following table:—

Temperature.	Density of saturated vapour (H = 1).	Ratio of actual to theoretical vapour density.
220·0°	53·5	1·786
230·0	54·3	1·815
240·0	55·3	1·847
250·0	56·5	1·889
260·0	58·3	1·947
270·0	60·3	2·016
280·0	63·1	2·108
290·0	67·1	2·241
300·0	73·3	2·450
310·0	83·5	2·791
320·0	112·4	3·754
321·65°	137·7	5·792

In a paper shortly to be read before the Physical Society, I have shown that at the critical point the ratio of the actual to the theoretical vapour density is for a considerable number of substances about 4·4. The very high ratio for acetic acid seems to show that at the critical point complex molecules are still present in considerable numbers.

That not only the saturated vapour of acetic acid, but also the liquid, is in a highly condensed state, probably owing also to the presence of complex molecules, seems to be indicated by the following considerations:—

If the generalisations of Van der Waals regarding corresponding temperatures, pressures, and volumes were strictly true, it would follow that the ratios of the molecular volumes, both of liquid and saturated vapour, of any two substances at corresponding pressures should be directly proportional to their absolute critical temperatures, and inversely to their critical pressures, or—

$$\frac{v}{v'} = \frac{V}{V'} = \frac{T.p'}{T'.p},$$

where v and v' are the molecular volumes of saturated vapour and V and V' the molecular volumes of liquid at corresponding pressures. Now, although this relation is by no means strictly true, yet if we take the mean ratios of the molecular volumes at a number of corresponding pressures, the differences between the three values $\frac{v}{v'}$, $\frac{V}{V'}$ and $\frac{T.p'}{T'.p}$, do not exceed 15 per cent. in the majority of cases examined, but when acetic acid is compared with fluorobenzene (which has usually been taken as the standard substance) the difference is no less than 40 per cent., the actual values for $\frac{\text{acetic acid}}{\text{fluorobenzene}}$ being $\frac{v}{v'} = 0·593$; $\frac{V}{V'} = 0·634$; $\frac{T.p'}{T'.p} = 0·830$.

The actual ratios for a number of corresponding pressures are given in the table below.

Pressures.		$\frac{v}{v'}$	$\frac{V}{V'}$	Pressures.		$\frac{v}{v'}$	$\frac{V}{V'}$
C_6H_5F.	$C_2H_4O_2$.			C_6H_5F.	$C_2H_4O_2$.		
20	25·6	—	0·6324	8000	10238	0·588	0·6349
50	64·0	—	0·6324	10000	12798	0·596	0·6348
100	128·0	—	0·6327	12000	15357	0·599	0·6350
200	256·0	—	0·6336	15000	19197	0·607	0·6335
400	511·9	—	0·6345	20000	25596	0·622	0·6331
760	972·6	—	0·6358	25000	31995	0·623	0·6319
1000	1280·0	0·545	0·6362	28000	35834	0·622	0·6342
1500	1920·0	0·552	0·6366	30000	38394	0·630	0·6321
2000	2560·0	0·557	0·6364	32000	40953	0·625	0·6311
3000	3839·0	0·565	0·6363	33912	43400	0·631	0·6310
4000	5119·0	0·571	0·6357				
5000	6399·0	0·577	0·6359				
6000	7679·0	0·582	0·6354		Mean..	0·593	0·6342
7000	8959·0	0·584	0·6353				

The molecular volumes of acetic acid both in the liquid state and as saturated vapour appear to be abormally low, and with the saturated vapour this is especially the case at low temperatures and pressures, for the ratio v/v' increases from 0·545 at a pressure (for fluorbenzene) of 1 metre to 0·631 at the critical point, whereas the ratio V/V' varies only between 0·6366 and 0·6309 within considerably wider limits of pressure.

LXXXI.—*On the Vapour Pressures and Molecular Volumes of Carbon Tetrachloride and Stannic Chloride.*

By Sydney Young, D.Sc., Professor of Chemistry, University College, Bristol.

Two years ago I read before the Chemical Society an account of experiments on the vapour pressures and molecular volumes in the liquid state of benzene and its four monohalogen derivatives (Trans., 1889, 55, 486) and last year I described the results of determinations of the molecular volumes of the saturated vapours of these substances (this vol, p. 125). These experiments were undertaken "in order to find whether the ratios of the boiling points (in absolute temperatures) of similar compounds of elements which belong to the same group in the periodic table are constant at all equal pressures, and whether any such simple relation holds good for the molecular volumes."

This was found to be the case for the four halogen derivatives of benzene, and it was further discovered that the critical pressures of these substances are equal or very nearly so. It follows from this that Van der Waals' generalisations regarding "corresponding" temperatures, pressures, and volumes are very nearly true for these bodies, but in this case "corresponding" pressures become equal pressures.

Since the publication of the first of these papers, I have been engaged in a study of the vapour pressures and molecular volumes of the chlorides of the elements of the carbon and silicon group, but since carbon tetrachloride acts on mercury at high temperatures, whilst stannic chloride causes it to adhere to glass even at the ordinary temperature, it was necessary to introduce several modifications into the methods of observation. This has caused considerable delay in the work, and I propose now to describe the results obtained with carbon tetrachloride and stannic chloride, reserving a discussion of the data until the completion of the investigation.

The chlorides were procured from Kahlbaum; the carbon tetrachloride was fractionated until a product of perfectly constant boiling point was obtained; the stannic chloride was extremely pure, but the first portions of the distillate contained a little hydrate, after the removal of which the liquid boiled quite constantly.

The following determinations of boiling point were made at various times.

Carbon tetrachloride.			Stannic chloride.		
Pressure.	Boiling point.	Corrected to 760 mm.	Pressure.	Boiling point.	Corrected to 760 mm.
750·1	76·3	76·7	756·7	113·9	114·05
756·0	76·55	76·7	764·4	114·3	114·1
748·0	76·25	76·75	759·1	114·1	114·15
768·25	77·2	76·85	755·0	113·9	114·15
768·25	77·05	76·7	741·2	113·15	114·0
771·4	77·3	76·8	748·9	113·6	114·1
766·4	77·0	76·75	756·8	113·9	114·05
762·8	76·75	76·65	759·4	114·1	114·15
760·3	76·75	76·75		Mean....	114·1
	Mean....	76·75			

Determinations of Boiling Point by other Observers.

Carbon Tetrachloride.

Pierre, *Compt. rend.*, **27**, 213, 78·1° at 748·3 mm. = 78·6° at 760 mm.
Regnault, *Mém. de l'Acad.*, **26**, 658 .... 76·5 „
Haagen, *Pogg. Ann.*, **131**, 117, 75·5° at 739·4 mm. = 76·4 „
Thorpe, *Trans. Chem. Soc.*, 1880, **37**, 59.......... 76·74 „
Perkin, „ „ 1884, **45**, 532 .... 76·9 „
Pawlewski, *Ber.*, **16**, 2633 .... 75·4 „
Schiff, *Annalen*, **223**, 72, 75·2° at 751·4 mm..... = 75·55 „

Stannic Chloride.

Haagen, *Pogg. Ann.*, **131**, 117, 112·0° at 754·9 mm.................................... = 112·25 at 760 mm.
Andrews, *Chem. News*, **25**, 61, 112·5° at 752 mm. .... = 112·9 „
Thorpe, *Trans. Chem. Soc.*, 1880, **37**, 331 ...... 113·9 „
Pierre, *Ann. Chim. Phys.* [3], **20**, 58, 115·4° at 753·1 mm............................. = 115·4 „

It will be seen that in both cases my results agree very closely indeed with Thorpe's.

Specific Gravity.

The specific gravity of carbon tetrachloride was determined in a Sprengel tube of the form recommended by Perkin; the weighings were reduced to a vacuum. The method is not applicable to stannic chloride on account of its extremely hygroscopic nature, and the specific gravity observed by Thorpe (Trans., 1880, **37**, 89), 2·27875 at 0°, was adopted in the calculations.

Carbon Tetrachloride.

Specific gravity at	0°.......	1·63255
„	15°........	1·6036 (from curve)
„	17·69°.....	1·59852
„	25°.......	1·5841 (from curve)

Determinations of Specific Gravity by other Observers.

Thorpe		1·63195 at 0°
Pierre		1·62983 „
Haagen..........	1·5947 at 20° =	1·6338 „
Schiff............	1·6084 at 9·5° =	1·6270 „
Perkin	1·60362 at 15° =	1·6330 „
„	1·58415 at 25° =	1·6330 „

My results at 15° and 25° are identical with Perkin's, and at 0° the agreement with Thorpe's determination is very satisfactory.

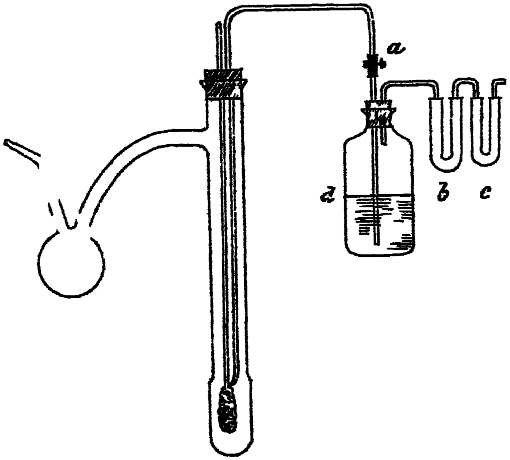
Vapour Pressures at Low Temperatures.

For carbon tetrachloride the method described by Ramsay and myself (Trans., 1885, **47**, 42) was available without modification, but the ordinary arrangement for delivering the liquid on to the cotton-wool could not be adopted in the case of stannic chloride on account of its extremely hygroscopic nature.

The method employed is shown in the diagram, Fig. 1 (next page).

At first a stopcock was fused to the glass at *a*, and was lubricated with partially deliquesced phosphorus pentoxide, but it was found that the oxide became very hard, owing apparently to removal of water by the stannic chloride, so that after a time the stopcock could not be turned. The indiarubber tube and screw clip shown in the diagram were therefore employed in place of the stopcock. The bottle *d* contains the stannic chloride, and the U-tubes *b* and *c* phosphorus pentoxide and calcium chloride. It was also found in the first two series of determinations that a small quantity of vapour of stannic chloride reached the mercury in the gauge and caused it to adhere to the glass, so that it became very difficult to obtain accurate readings; in the third series, therefore, tubes containing dry potash, moist potash, calcium chloride, and phosphorus pentoxide were interposed between the still and the gauge. The vapour of stannic chloride passed freely over the dry potash, but was completely absorbed by the moistened alkali; the calcium chloride and phosphorus pentoxide prevented the passage of moisture to the gauge.

FIG. 1.



Carbon Tetrachloride.

Series I.

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
°	mm.	°	mm.	°	mm.	°	mm.
−18·1	11·25	−9·3	19·4	+0·05	33·0	13·2	65·35
−15·6	13·3	−7·0	22·45	2·9	38·35	16·95	77·7
−14·55	14·05	−4·5	25·7	5·35	44·0		
−11·95	16·7	−2·05	29·2	8·9	52·45		

Series II.

7·6	49·35	29·6	137·15	49·6	302·7	69·55	602·2
11·1	58·8	32·4	154·7	52·35	333·0	72·35	661·3
14·0	67·6	35·4	174·1	54·8	367·9	75·2	719·4
17·0	77·95	38·6	197·5	58·3	414·6	77·15	769·5
20·1	90·3	41·5	221·3	61·25	458·0		
23·1	103·65	43·85	243·4	64·25	503·4		
26·7	120·25	46·6	271·2	67·25	557·0		

Stannic Chloride.

Series I.

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
	mm.		mm.		mm.		mm.
−9°·55	2·5	−2°9	4 4	7°·1	8·8	18°·75	17·05
−7·9	3·1	−0·1	5 3	10·0	10·35	22·1	20·95
−7·1	3·15	+0·8	5·85	13·15	12·25		
−5·0	3·65	4 05	7 2	17·0	15·35		

Series II.

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
−3·7	4·1	15·0	13·9	34·15	38·8	52·8	90·85
+1·0	5·6	18·0	16·65	36·7	44·15	56·8	103·85
4·05	7·1	21·5	20·1	39·0	49·45	59·85	118·3
6·75	8·65	24·95	24·2	43·15	59·75	63·4	134·45
10·0	10·7	28·75	29·25	46·85	70·7	66·0	150·4
12·75	12·1	31·25	33·85	49·9	80·7	69·75	172·95

Series III.

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
−5·85	3·75	6·45	8·5	30·55	31·95	59·45	117·45
−4 55	4·05	10·7	11·0	35·7	41·5	65·25	148·1
−3·45	4·3	15 0	14·15	41·65	55·1	70·1	178·65
+0·05	5·35	20·7	19·3	47·7	71·65		
2·45	6·6	25·4	24·75	53·5	91·9		

The boiling points at higher pressures were determined in the ordinary manner, a thermometer being suspended in the vapour from the boiling liquid.

Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
	mm.		mm.		mm.		mm.
71°·7	193·95	79°·55	257·75	92°·35	395·9	105°85	596·8
73·8	209·3	82·7	287·1	96·15	445·7	108·6	648·9
75·5	222·1	85·6	317·3	99·7	496·0	111·5	705·3
76·6	231·95	88·65	352·4	102·65	544·5	114·1	760 2

The logarithms of the pressures were mapped against temperature and the values corresponding to even temperatures read from the curves. The pressures corresponding to the smoothed logarithms are given in the final tables.

Vapour Pressures at High Temperatures.

A series of determinations with carbon tetrachloride was made in the ordinary manner in the modified Andrews' apparatus, but it was found that even at 150° a small quantity of black substance formed on the sides of the tube and was carried down by the mercury when the volume was increased. This took place even when the tube was shielded from the light.

At higher temperatures the decomposition took place to a greater extent, and after heating to the critical point the carbon tetrachloride had become slightly brown, and on cooling deposited a considerable quantity of long, needle-shaped crystals. There was also a small bubble of gas which could be dissolved only under high pressure.

After heating the chloride to 230°, determinations were repeated at 110° and 120° in order to find whether the vapour pressure had been influenced by the decomposition. It will be seen from the table of results that no alteration had taken place, so that the pressures up to 230° may be taken as correct. A similar repetition, however, after the determination of the critical point, gave distinctly lower pressures, notwithstanding the presence of a small quantity of gas. Above 230°, therefore, the data must be considered doubtful, and at the critical point there is certainly a considerable error.

Vapour Pressure of Carbon Tetrachloride in contact with Mercury.

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
90°	1109 1113 1112 1113	1112	130°	3011 3008 3008 3011	3009
100°	1459 1456 1457 1456	1457	140°	3728 3725 3722 3727	3725
110°	1882 1879 1880 1881	1880	150°	4552 4552 4550	4551
120°	2394 2390 2390 2392	2391	150°	4564 4560 4557	4560
130°	2998 2995 2995 2994	2995	160°	5544 5539 5533	5539

Vapour Pressure of Carbon Tetrachloride in contact with Mercury.

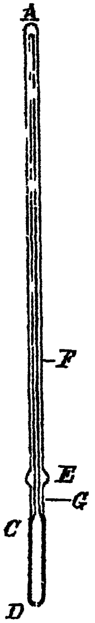
Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
170°	6645 6634 6644	6641		Doubtful.	
180°	7903 7896 7897	7899	240°	19593 19599 19594	19595
190°	9307 9304 9307	9306	250°	22430 22405 22423	22420
200°	10938 10941 10937	10939	260°	25513 25487 25479	25493
210°	12776 12751 12751	12759	270°	28967 28931 28909	28936
220°	14799 14802 14797	14799	279·7	32484 32500	32492
230°	17057 17050 17050	17052	284·4°	—	34358
			284·6° (apparent critical point)	—	34412
110°	1879 1879 1879	1879	110°	1876 1879 1872	1876
120°	2392 2390 2390	2391	120°	2373 2370 2373	2372

In order to obtain accurate results at the highest temperatures, it is evidently necessary that the mercury, if present, should not be heated. The difficulty was overcome by enlarging the vapour pressure tube at its lower open end, as shown in Fig. 2 (p. 918), and increasing the quantity of carbon tetrachloride, so that the mercury should always be in the cold part of the apparatus.

The enlargement at E serves to keep the tube firmly fixed in the pressure apparatus.

The whole tube, including the cylindrical bulb DC, was graduated in millimetres, and calibrated by weighing with mercury. In the case of a tube of narrow bore throughout, the fact that the meniscus of the mercury during calibration is in the reverse position from that during the actual experiments is of little importance; for the volume may be corrected with very slight error on the assumption that the surface of the mercury forms a hemisphere. With a tube of the form described, however, such a simple correction could not be made, and the end D was therefore temporarily closed, and A opened. After the calibration, the end A was sealed again and D opened, and a little mercury was then admitted into the narrow part of the tube, the reading taken, and the mercury removed and weighed. The correction for the reversal of the meniscus was then made in the ordinary way, and the true volume at this division of the tube was thus ascertained. The volumes corresponding to the previous readings were then easily calculated. The tube was filled in the usual manner, but a larger quantity of liquid was admitted, the amount being so regulated that in the determinations of vapour pressure the surface of the mercury was always below the conical part C of the wider tube. The position of the vapour pressure tube and the air gauges in the pressure apparatus is shown diagrammatically in Fig. 3, which represents a vertical cross section.

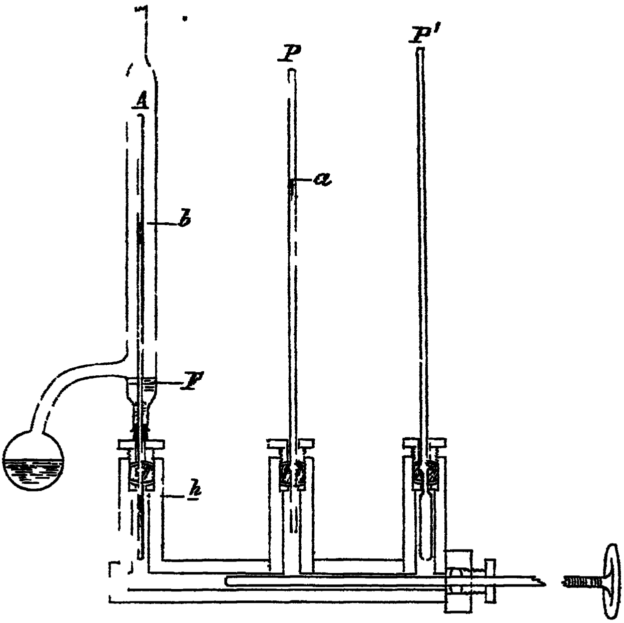
FIG. 2.



The pressure in the air manometer P on the surface of mercury

a is calculated in the usual manner from the volume and temperature of the air, and it must be corrected for the deviation of air from Boyle's law.

FIG. 3.



The vapour pressure of the substance, that is, the pressure on the surface of the liquid b, however, is different. To the pressure, as measured by the air gauge, must be added that of the column of mercury between the levels a and h, while the pressure of the column of liquid bh must be subtracted from it. There is also a small correction for capillarity, amounting in this case to 3 mm.

1. Calculation of level of mercury h.

During any experiment, the portion of the tube from A to F (Figs. 2 and 3) is heated to T°, the remainder of the tube being at the ordinary temperature $t°$, which may with sufficient accuracy be taken always as 20°.

When AF is at 0°, and the lower part of the tube at 20°, let the junction of mercury and liquid be at G (Fig. 2). Let v be the volume from A to F, and u the volume from F to G.

Taking the specific volume of the liquid at 0° as unity, let that at $T° = 1 + x$, and at $20° = 1 + y$.

When the tube from A to F is heated to T°, and the vapour is just condensed, the liquid which occupied the volume v at 0° will have expanded and will now become $v + \frac{vx(1+y)}{1+x}$, and the total volume of liquid will be

$$v + u + \frac{vx(1+y)}{1+x}.$$

When the liquid is drawn down so that n divisions of the tube are occupied by saturated vapour, the total volume of liquid and vapour will be

$$v + u + \frac{(vx + nz)(1+y)}{1+x},$$

where z is the volume corresponding to one scale division.

This calculation neglects the loss of liquid by conversion into saturated vapour, but the error would in no case be large.

It would be greatest close to the critical point (at which the specific volumes of vapour and liquid are equal), and when the upper surface of the liquid is at its lowest point F. It is assumed in the calculation that when the volume is increased so as to bring down the upper surface of the liquid to, say, the position F, the whole of the liquid is drawn down into the lowest part of the tube, whereas in this case there is really a very minute increase of volume, the liquid being for the most part converted into vapour. The maximum error in volume, therefore, will be $\frac{v(1+y)}{1+x}$, or, roughly, $0{\cdot}4v$. Calculated as length, the error will be very small, since the movement of the mercury is in the wide cylindrical tube and not in the narrow barometer tube. In the longer of the two tubes employed, the length AF, corresponding to the volume v, was 335 mm., and the ratio of the area of the cross section of the barometer tube to that of the cylinder was about $\frac{1}{6}$, so that the approximate maximum error would be $\frac{335 \times 0{\cdot}4}{6} = 22$ mm., and this would be still further diminished by the compensating error in the calculation of the pressure of the column of liquid.

With a critical pressure of 22,000 mm., lower than any yet observed, the maximum error could not therefore amount to so much as 0·1 per cent., and as the liquid was never drawn down so low as F, the actual error in the worst case must have been still smaller, and at temperatures not very near to the critical point was quite negligible.

The error due to the expansion of the glass is too small to be taken into consideration.

As readings were taken with the upper surface of the liquid at the same scale divisions at each temperature, it was possible to construct curves for definite values of n and varying values of x by means of which the labour of correction was greatly reduced.

Having found the total volume of liquid and vapour at each reading of pressure, it was easy to determine the level h of the mercury in the tube by means of a diagram showing the volumes corresponding to each scale division, and the correction due to the difference of level of the mercury in the air manometer and vapour pressure tube was thus ascertained.

The next point is the determination of the pressure of the column of liquid above the mercury.

Let S_T be the specific gravity of the liquid at T°, and S_{20} at 20°, and let the level of the mercury h (already calculated) be m mm. below F at any reading; also let l be the length AF of the heated portion of the tube. When the vapour is completely condensed, the pressure in millimetres of mercury due to the column of liquid will be

$$p = \frac{l \, . \, S_T + m \, . \, S_{20}}{13{\cdot}6},$$

and when the upper surface of the liquid is n divisions below the top of the tube, the pressure will be

$$p' = \frac{(l - n)S_T + m'S_{20}}{13{\cdot}6}.$$

Here, again, by suitable construction of curves, or rather straight lines, the labour of correction is greatly lightened. Those constructed were:—

(1.) For the factor $\frac{(l - n)S_T}{13{\cdot}6}$ for definite values of n and varying values of S_T.

(2.) For the factor $\frac{mS_{20}}{13{\cdot}6}$ for varying values of m.

The correction for capillarity was, as already stated, 3 mm.

In order to test the accuracy of the method, determinations of vapour pressure of carbon tetrachloride were made at several temperatures both by this and by the ordinary method. The comparison is given in the following table:—

Temperature.	Mean vapour pressures. New method.	 Old method.
190°	9316	9306
200	10933	10939
210	12759	12759
220	14792	14799
230	17060	17052

The agreement, it will be seen, is remarkably close.

Determinations of Vapour Pressure by New Method.
Carbon Tetrachloride.

Temp.	Pressure.	Mean.
190°	9316	9316
	9319	
	9317	
	9324	
	9312	
	9311	
200°	10934	10933
	10930	
	10931	
	10936	
210°	12769	12759
	12757	
	12755	
	12757	
220°	14799	14792
	14798	
	14791	
	14780	
230°	17066	17060
	17060	
	17056	
	17058	
240°	19633	19633
	19639	
	19626	
	19633	
250°	22430	22414
	22404	
	22394	
	22427	
260°	25531	25528
	25526	
	25533	
	25521	
270°	29003	28991
	28993	
	28990	
	28978	
280°	32854	32825
	32825	
	32808	
	32812	
283·05°	34148	34133
	34149	
	34127	
	34109	
283·15° (critical point)	34181	—

After being heated to the critical point, the liquid remained perfectly clear and colourless, so that no decomposition had taken place. It has been pointed out that the pressures by the two methods agree perfectly well up to 230°; at 240°, there is a difference of 38 mm.; but at 250°, the agreement is again perfect. Above this temperature there is a continually increasing difference, amounting at 280° to over 200 mm. (allowing for the slight difference of temperature). Moreover, the critical point now observed is 283·15° instead of 284·6° by the old method. There can be no doubt that the new results are more trustworthy, and there does not appear to be any source of error affecting them.

Stannic Chloride.

It has been already stated that stannic chloride attacks mercury at low temperatures, spoiling its surface, and causing it to adhere to glass. If, however, some stannic chloride is admitted carefully into a vessel containing mercury, there is no apparent effect so long as the metal remains perfectly still, but on tilting the vessel, it is found that a thin film has been formed on the surface of the mercury, and if the two liquids are shaken vigorously together, the mercury breaks up into innumerable globules, some of them so fine that they remain suspended in the stannic chloride for a considerable time. It does not appear, however, that there is any appreciable chemical action between the two substances even at 114°, for on distilling some stannic chloride with a little mercury, the boiling point was quite unaffected, and when the finely divided grey powder remaining in the distillation bulb was boiled with hydrochloric acid, the particles reunited to form a bright globule of metallic mercury, and none of the metal could be detected in the solution in the form of chloride.

Contact with mercury at low temperatures does not, therefore, injure stannic chloride, and the vapour pressures may therefore be determined by the new method.

Special precautions were taken to avoid the presence of moisture in the stannic chloride. A current of air, dried over phosphorus pentoxide, was passed through the distillation bulb before the insertion of the liquid, and the vessels in which the distillate was collected were similarly freed from moisture. The chloride was transferred from the bottle containing it into the distillation bulb by means of a siphon, the short end of which passed through a doubly perforated india-rubber cork fitting the bottle. Through the second hole in the cork passed a short glass tube, connected with U-tubes containing calcium chloride and phosphorus pentoxide, so that only dry air entered the bottle. As in the case of acetic acid, the distillate was collected directly in the little glass vessel from which the vapour-pressure tube was filled, and the glass vessel was placed in a drying chamber containing dishes of sulphuric acid and of phosphorus pentoxide. A hole about an inch wide was made in the side of the drying chamber, and was closed by a piece of sheet india-rubber fastened to the side of the chamber by means of india-rubber solution. The delivery tube from the distillation bulb passed through a perforation in the sheet india-rubber into the drying chamber, which was provided with a well-fitting glass door for the insertion or removal of the vessels in which the distillate was collected.

Similar precautions were taken in filling the tubes employed for the determination of the specific volumes of stannic chloride.

Series I.

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
130°	1171 1172 1171 1170	1171	220°	7264 7254 7254 7247	7255
140°	1498 1497 1496 1497	1497	230°	8477 8474 8469 8465	8471
150°	1893 1892 1892 1893	1892	180°	3556 3554 3551 3554	3554
150°	1901 1896 1896 1895	1897	240°	9922 9911 9906 9922	9915
160°	2371 2369 2368 2368	2369	250°	11528 11529 11522 11519	11524
170°	2921 2921 2925 2933	2925	260°	13316 13306 13304 13304	13307
180°	3560 3556 3554 3554	3556	270°	15300 15291 15288 15283	15290
190°	4292 4284 4282 4282	4285	279·5°	17372 17361 17359 17359	17363
200°	5154 5146 5144 5142	5146	180°	3558 3559 3557 3555	3557
210°	6121 6123 6118 6114	6119			

There was a slight white deposit on the sides of the tube; it was noticed first at 200°, and increased slightly at higher temperatures. The redeterminations at 180°, after heating to 230° and 279·5°, were made in order to find whether the vapour pressure had been affected by the formation of the deposit.

The concordance is so close that it may be concluded that the slight decomposition was without influence.

With short Vapour Pressure Tube.

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
150°	1898 1898 1897 1895	1897	240°	9919 9917 9912 9911	9915
160°	2367 2369 2366 2367	2367	250°	11503 11508 11504 11507	11504
170°	2916 2917 2915 2915	2916	260°	13274 13275 13272 13276	13274
180°	3557 3556 3555 3554	3555	270°	15273 15265 15266 15271	15269
190°	4285 4287 4282 4281	4284	280·2°	17496 17492 17486 17490	17491
200°	5149 5149 5139 5137	5143	309·5°	24935 24931 24912 24930	24927
210°	6119 6115 6110 6111	6114	319·35° (critical point)	28079	28079
220°	7217 7222 7223 7227	7222	180°	3554 3557 3557 3556	3556
230°	8478 8476 8480 8488	8480			

The repetition at 180° shows that no appreciable amount of decomposition had taken place.

This work was carried out before the addition of dibenzyl ketone to the list of heating agents, and mercury vapour was therefore employed as a jacket for the two highest temperatures.

The data are corrected in accordance with the recalculated vapour pressures of mercury (this vol., p. 629).

Constants for Biot's formula, $\log p = a + b\alpha^t + c\beta^t$, were calculated for the two substances; they are:

Carbon Tetrachloride.

$$a = -1{\cdot}50723;$$

$\log b = 0{\cdot}7162086;$ $\log c = 0{\cdot}3375918;$

$\log \alpha = 0{\cdot}00026855;$ $\log \beta = \bar{1}{\cdot}99597566;$

c is negative; $t = t^\circ$ C.

Vapour Pressures of Carbon Tetrachloride.

Temperature.	Observed pressure.	Calculated.	Δ.	Regnault.
	Mean.			
−20	9·92	10·29	+ 0·36	9·80
−10	18·81	18·89	+ 0·08	18·47
0	33·08	33·08	0	32·95
10	55·65	55·51	− 0·14	55·97
20	89·55	89·61	+ 0·06	90·99
30	139·6	139·64	+ 0·04	142·27
40	210·9	210·71	− 0·19	214·81
50	309·0	308·09	− 0·91	314·38
60	439·0	440·67	+ 1·67	447·43
70	613·8	613·8	0	621·15
80	—	836·35	—	843·29
90	1112·0	1117·0	+ 5·0	1122·26
100	1457·0	1464·8	+ 7·8	1467·1
110	1880·0	1889·4	+ 9·4	1887·4
120	2391·0	2400·8	+ 9·8	2393·7
130	3002·0	3009·1	+ 7·1	2996·9
140	3725·0	3725·1	+ 0·1	3709·0
150	4555·0	4559·6	+ 4·6	4543·1
160	5539·0	5524·6	−14·4	5513·1
170	6641·0	6631·9	− 9·1	6634·4
180	7899·0	7894·8	− 4·2	7923·6
190	9311·0	9326·7	+15·7	9399·0
200	10936·0	10943·0	+ 7	—
210	12759·0	12759·0	0	—
220	14795·0	14793·0	− 2	—
230	17056·0	17066·0	+10	—
240	19633·0	19596·0	−37	—
250	22414·0	22409·0	− 5	—
260	25528·0	25532·0	+ 4	—
270	28991·0	28992·0	+ 1	—
280	32825·0	32825·0	0	—

Stannic Chloride.

$$a = 1{\cdot}19484;$$

$$\log b = 0{\cdot}6824293; \qquad \log c = 0{\cdot}4546821;$$

$$\log \alpha = 0{\cdot}00026212; \qquad \log \beta = \bar{1}{\cdot}99631718;$$

c is negative; $t = t^{\circ}$ C.

In the tables on pp. 926 and 927 the vapour pressures calculated from these constants are given, together with the mean observed pressures, and in the case of carbon tetrachloride the pressures observed by Regnault.

Vapour Pressures of Stannic Chloride.

Temperature.	Observed pressure.	Calculated.	Δ.	Temperature.	Observed pressure.	Calculated.	Δ.
	Mean.				Mean.		
−10	2·78	3·08	+0·30	160·0	2368	2359	−9
0	5·53	5·88	−0·35	170 0	2920	2914	−6
10	10·33	10·72	+0·39	180 0	3555	3561	+6
20	18·58	18·72	+0·14	190·0	4284	4309	+25
30	31·30	31·42	+0·12	200·0	5145	5168	+23
40	50·82	50·88	+0·06	210·0	6116	6147	+31
50	79·80	79·68	−0·12	220·0	7238	7257	+19
60	122·2	121·1	−1·1	230 0	8475	8509	+34
70	178·9	178·8	−0·1	240·0	9915	9915	0
80	256·7	257·5	+0 8	250·0	11514	11488	−26
90	360·6	362·2	+1·6	260·0	13290	13242	−48
100	496·0	498·5	+2·5	270·0	15280	15190	−90
110	675·3	672·7	−2·6	280·0	17454	17351	−103
120	895·4	891·4	−4·0	290 0	—	19742	—
130	1171·0	1162·0	−9·0	300·0	—	22382	—
140	1497·0	1491·0	−6·0	310·0	25079*	25294	+215
150	1895·0	1888·0	−7 0	319·35	28079	28283	+204

Critical Temperatures and Pressures.

Carbon Tetrachloride.

At 283·8° there was no meniscus; striæ were seen on increasing the volume, followed by a mist in the tube.

At 283·55° no meniscus was visible; on increasing the volume, a dense mist was formed, and remained for some time.

At 283·3° there was still no meniscus, but the mist was denser.

At 283·05° a meniscus was visible; on diminishing the volume, the tube became clear at first, but very soon a dense mist and striæ were formed, after which the meniscus slowly reappeared.

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* Calculated from observation at 309·5°.

At 283·15° the meniscus appeared after increasing the volume, but soon gave place to dense mist. On decreasing the volume, the tube cleared, and the mist reappeared only slowly.

The critical temperature of carbon tetrachloride is therefore 283·15°, and the critical pressure 34180 mm.

Pawlewski (*Ber.*, 16, 2633) gives the critical temperature 285·3°, while Dewar finds the temperature 282°, and the pressure 57·6 atmos.

Stannic Chloride.

Mercury vapour is not well suited for a jacketing substance, for the liquid condenses in small globules on the sides of the tube, obscuring the view, and also the temperature is not quite steady, and is a little lower at the bottom of the tube than at the top.

At 319·15° there was a distinct meniscus.

At 319·3° the meniscus was just permanent.

At 319·35° the meniscus was only visible at times, but there was a dense mist.

At 319·5° the meniscus could be obtained for a moment by suddenly increasing the volume, but it rapidly disappeared.

At 319·8° it was impossible to produce even a temporary meniscus.

The apparent critical temperature is 319·35°, but it will be noticed in the table of vapour pressures that the calculated vapour pressure for 319·35° is 204 mm. higher than the observed critical pressure. As there is no reason to suspect any error in the determination of the critical pressure, while the temperature is a little uncertain owing to the employment of mercury vapour as a jacket, it seems best to take the pressure as correct, and to calculate the temperature corresponding to this pressure by means of Biot's formula. This would make the critical constants

Temperature	318·7
Pressure	28080

Volumes of a Gram and Molecular Volumes of Liquids.

Carbon Tetrachloride.

It has been already mentioned that carbon tetrachloride undergoes some decomposition when heated with mercury, but it was found that so long as the two liquids were only in contact at the curved surface of the meniscus the action was very slight; it was far greater where there was a film of the tetrachloride between the mercury and the glass. By keeping the liquid always condensed in the modified Andrews' apparatus, and taking readings always at increasing temperatures, the formation of this film could be almost entirely prevented, and it was thus possible to obtain trustworthy readings up to within a moderate distance of the critical point.

The results are given in the table under the heading "old method."

In the first series, the readings are only given up to 130°, for above that temperature the mercury was repeatedly drawn down the tube for the determinations of vapour pressure. In the second series, the volumes of a gram only were determined.

Weights of Substance.

I. The observed volumes were mapped, and the volumes corresponding to 0° and 17·7° read from the curves. The weight was calculated from these volumes and the known specific gravities, and was found to be (1) 0·7258, (2) 0·7257; mean, 0·72575.

II. The volumes at 90°, 100°, 110°, 120°, and 130° were compared with those of the first series. The ratios of the old to the new volumes were: 1·673, 1·674, 1·673, 1·673, 1·676; mean, 1·674. The weight was therefore 0·4336.

Note on Series II.—On raising the temperature above 280°, the carbon tetrachloride was so much acted on that the results could not be relied upon; the temperature was, however, raised to the critical point. The volumes at 100° and 110° were redetermined after the liquid had been heated to 230°, and again after the critical point had been reached. In the first case there was no change of volume, but in the second there was a contraction of about 1·5 per cent. The results are therefore certainly trustworthy up to 230°, and the error at 280° is probably not large, for the decomposition was greatest between this temperature and the critical point.

In the early part of this volume of the Transactions, p. 37, I described a new method of determining the specific volumes of liquids and saturated vapours suitable for substances that attack mercury. The results obtained by this method are given under the heading "new method," I.

The chief objection to the new method is the expenditure of time involved in pushing up the volume tube into the hot vapour at each temperature. The necessity for doing this may, however, be avoided by making two sets of determinations of apparent volumes of liquid and saturated vapour *with the whole tube heated*, varying the relative volumes of liquid and vapour in the two series as much as possible.

Having determined the actual weights of substance present, the read volumes of liquid and vapour are reduced to what they would be if 1 gram of substance were employed in each series, the tubes being assumed to be altered in size so that the relative volumes of liquid and vapour remain unaltered. Let the reduced volumes of liquid be Va and $V'a$, and of vapour Vb and $V'b$.

Then while R, the ratio of the specific volume of saturated vapour to that of liquid, and V, the true volume of a gram of liquid, will of course be the same in both series, Va and Vb will differ from $V'a$ and $V'b$.

We shall then have
$$R = \frac{Vb}{V-Va} = \frac{V'b}{V-V'a},$$
from which
$$V = \frac{VaV'b-V'aVb}{V'b-Vb}.$$

Lastly, the volume of a gram of saturated vapour = RV. In some respects this method is preferable to the other, for, though it involves two separate series of determinations, the readings can be taken very much more rapidly, the position of the volume tube remaining unaltered during the experiments with each jacketing substance.

Two series of observations were made with carbon tetrachloride with different tubes, and the volumes of a gram of liquid were calculated from these results, together with those of the first series, taking only the readings when the whole tube was heated.

The data are given in the table under the headings "New method," II and I, and III and I (p. 932).

In the case of stannic chloride, two series of determinations, I and II, were made by the new method in its original form, and two more, III and IV, with the whole tube always heated.

In calculating the molecular volumes, the molecular weights were taken to be—

$$CCl_4 = 153{\cdot}45, \qquad SnCl_4 = 259{\cdot}3.$$

The weights of substance were determined by observing the volume at 0°, and at one or two other temperatures, correcting them when necessary for the amount of substance present as saturated vapour, and multiplying the corrected volumes by the specific gravities at the same temperatures. For stannic chloride, Thorpe's data were employed.

Weights of Substance.

Carbon Tetrachloride.

	Temperature.	Volume.	Corrected.	Weight.
I	16·25°	0·4568	0·4572	0·7317
II	0	0·1505	0·1509	0·2464
	17·30	0·1533	0·1543	0·2468
			Mean	0·2466
III	0	0·1226	0·1227	0·2002
	17·60	0·1249	0·1251	0·2000
			Mean	0·2001

Stannic Chloride.

	Temperature.	Volume.	Corrected.	Weight.
I	16·8°	0·5391	0 5392	1·2050
II	0	0·5082	0·5082	1·1581
	13 5	0 5162	0·5163	1·1582
			Mean	1·1581
III	0	0·1677	0·1678	0·3824
	17 4	0·1714	0·1716	0·3832
	19·2	0·1715	0 1718	0·3828
			Mean	0·3828
IV	0	0·1280	0·1280	0·2917
	19·0	0·1308	0·1309	0·2917
			Mean	0·2917

The determinations of the volumes of a gram and molecular volumes are given in the following tables :—

Carbon Tetrachloride.

Temp.	Volumes of a gram.						Molecular volumes.
	Ordinary method.	New method.					
		I.	II and I	III and I.	Mean.	From curve.	
0°	(0·61254)	—	—	—	0·6125	0·6125	93·99
10	—	—	—	—	—	0·6199	95·12
20	—	—	—	—	—	0·6274	96·27
30	0·6357	—	—	—	0·6357	0·6350	97·44
40	0·6430	—	—	—	0·6430	0·6428	98·64
50	0·6508	—	—	—	0·6508	0·6510	99·90
60	0·6592	—	—	—	0·6592	0·6594	101·19
70	0·6682	—	—	—	0·6682	0·6683	102·55
80	0·6773	—	—	—	0·6773	0·6773	104·09
90	0·6869	—	—	—	0·6869	0·6871	105·44
100	0·6973	0·6961	0·6972	—	0·6969	0·6972	106·99
110	0·7075	—	0·7082	—	0·7078	0·7080	108·64
120	0·7190	—	0·7195	—	0·7192	0·7193	110·38
130	0·7320	—	0·7312	—	0·7316	0·7310	112·17
140	—	—	—	—	—	0·7435	114·09
150	0·7567	0·7539	—	0·7590	0·7565	0·7567	116·12
160	0·7701	0·7676	—	0·7723	0·7700	0·7703	118·20
170	0·7856	0·7852	—	0·7883	0·7864	0·7853	120·51
180	0·8024	0·7997	—	0·8045	0·8022	0·8019	123·05
190	0·8200	0·8175	—	0·8222	0·8199	0·8202	125·86
200	0·8416	0·8418	—	0·8417	0·8417	0·8412	129·08
210	0·8640	0·8664	—	0·8661	0·8655	0·8646	132·68
220	0·8896	0·8899	—	0·8926	0·8907	0·8907	136·68
230	0·9197	0·9219	—	0·9224	0·9213	0·9211	141·34
240	0·9566	—	—	0·9595	0·9580	0·9575	146·93
250	0·9980	1·0029	—	1·0055	1·0021	1·0021	153·77
260	1·059	1·0660	—	1·0636	1·0629	1·0628	163·09
270	1·148	—	—	—	1·148	1·154	177·10
280	1·310	—	—	—	1·310	1·310	200·10
14·55	0·6229	—	—	—	—	—	—
25·0	0·6313	—	—	—	—	—	—
269·1	—	—	—	1·148	—	—	—
275·0	1·211	—	—	—	—	—	—

Stannic Chloride.

Temp.	Volumes of a gram.							Mol. vols.
	I.	II.	II and III.	II and IV.	I and IV.	Mean.	From curve.	
0°	—	—	—	—	—	(0·4388)	0·4388	113·79
10	—	—	—	—	—	—	0·4440	115·13
20	—	—	—	—	—	—	0·4492	116·48
30	—	0·4545	—	—	—	0·4545	0·4545	117·85
40	—	0·4598	—	—	—	0·4598	0·4598	119·23
50	—	0·4654	—	—	—	0·4654	0·4654	120·68
60	—	0·4712	—	—	—	0·4712	0·4710	122·13
70	—	0·4767	—	—	—	0·4767	0·4768	123·63
80	—	0·4825	0·4824	—	—	0·4824	0·4827	125·16
90	—	0·4890	0·4890	—	—	0·4890	0·4890	126·80
100	—	0·4956	0·4955	—	—	0·4955	0·4954	128·46
110	—	—	0·5020	—	—	0·5020	0·5021	130·19
120	—	—	0·5092	—	—	0·5092	0·5092	132·04
130	—	0·5170	0·5168	—	—	0·5169	0·5166	133·95
140	—	0·5239	0·5243	0·5248	—	0·5243	0·5243	135·95
150	—	0·5320	0·5328	0·5332	—	0·5327	0·5327	138·13
160	—	0·5413	0·5415	0·5442	—	0·5417	0·5411	140·31
170	—	0·5491	0·5504	0·5510	—	0·5502	0·5500	142·61
180	—	0·5580	0·5602	0·5606	—	0·5596	0·5595	145·08
190	0·5678	—	—	—	0·5689	0·5683	0·5696	147·70
200	0·5811	—	—	—	0·5802	0·5806	0·5806	150·55
210	0·5917	—	—	—	0·5940	0·5929	0·5929	153·74
220	0·6053	—	—	—	0·6077	0·6065	0·6065	157·26
230	0·6207	—	—	—	0·6220	0·6213	0·6215	161·15
240	—	0·6385	—	0·6384	—	0·6385	0·6383	165·51
250	—	0·6570	—	0·6569	—	0·6570	0·6570	170·36
260	—	0·6780	—	0·6783	—	0·6781	0·6781	175·83
270	—	0·7034	—	0·7032	—	0·7033	0·7033	182·36
280	0·7330	0·7356	—	0·7333	0·7327	0·7336	0·7338	190·27

For the sake of comparison, it may be well to give the results obtained by other observers. As the volume at 0° is usually taken as unity, I have calculated my results on this basis.

Temp.	Carbon tetrachloride.				Stannic chloride.		
	Thorpe.	Pierre.	Hirn.	Young.	Thorpe.	Pierre.	Young.
10°	1·01215	—	—	1·0120	1·01168	—	1·0118
20	1·02452	1·02414	—	1·0243	1·02353	1·02308	1·0237
30	1·03718	—	1·0349	1·0367	1·03531	—	1·0358
40	1·05022	1·04966	—	1·0494	1·04771	1·04726	1·0479
50	1·06372	—	—	1·0628	1·06061	—	1·0606
60	1·07776	1·07719	—	1·0765	1·07341	1·07289	1·0738
70	1·09241	—	1·0891	1·0910	1·08706	—	1·0864
80	1·10777	—	—	1·1057	1·10080	1·10034	1·0994
90	—	—	—	1·1217	1·11532	—	1·1144
100	—	—	1·1359	1·1382	1·13024	1·12998	1·1292
110	—	—	1·1531	1·1558	1·14576	—	1·1440
120	—	—	1·1712	1·1743	—	—	—
130	—	—	1·1905	1·1934	—	—	—
140	—	—	1·2110	1·2138	—	—	—
150	—	—	1·2330	1·2354	—	—	—
160	—	—	1·2566	1·2576	—	—	—

It will be seen that my results are in fair accordance with those of Thorpe and Pierre. Hirn's determinations of the volumes of carbon tetrachloride appear to be too low.

Carbon Tetrachloride.

Temperature.	Volumes of a gram.			From curve.	Molecular volumes.
	I.	II.	III.		
90°	—	126·2	—	125·4	19250
100	—	97·4	—	97·5	14950
110	—	76·5	—	76·7	11750
120	—	60·8	—	61·2	9390
130	—	49·2	—	49·4	7590
140	—	—	—	40·3	6190
150	—	—	32·2	33·1	5080
160	28·0	—	27·4	27·4	4200
170	24·0	—	22·9	22·8	3500
180	19·7	—	19·10	19·05	2925
190	16·3	—	16·01	16·00	2456
200	13·6	—	13·48	13·48	2069
210	11·5	—	11·37	11·38	1746
220	9·70	—	9·59	9·62	1476
230	8·17	—	8·12	8·12	1246
240	6·86	—	6·80	6·83	1047
250	5·72	—	5·66	5·70	874
260	4·67	—	4·66	4·66	715
270	3·70	—	—	3·69	566
280	2·79	—	—	2·78	427

Volumes of a Gram and Molecular Volumes of Saturated Vapour.

These were determined by the new method; in calculating the ratios of the specific volumes of the saturated vapour to those of the liquid at each temperature by means of the formula $R = \frac{Vb}{V - Va}$, the values of V taken were those read from the curve.

The different series are numbered as in the tables of the volumes of liquid.

Stunnic Chloride.

Temp.	Volumes of a gram.					Molecular volumes.
	I.	II.	III.	IV.	From curve.	
100°	—	—	174·4	—	173·5	45000
110	—	—	131·5	—	131·0	34000
120	—	—	101·8	—	100·6	26100
130	—	—	77·5	—	78·4	20300
140	-	—	62·5	59·0	61·9	16100
150	—	—	49·6	47·9	49·4	12800
160	—	—	40·0	38·6	39·9	10340
170	—	—	32 54	31·8	32·5	8410
180	—	—	26·78	26·5	26·6	6910
190	21·6	—	—	22·2	22 0	5700
200	18·4	—	—	18·55	18·35	4760
210	15·9	—	—	15·30	15·38	3990
220	13·4	—	—	12·93	12·94	3355
230	11·0	—	—	10·87	10·93	2835
240	—	9·20	—	9·18	9 23	2393
250	—	7·78	—	7·79	7·81	2024
260	—	6·61	—	6·59	6·58	1706
270	—	5·53	—	5·55	5·52	1432
280	4·61	4·63	—	4 65	4·63	1200

It is obvious from the equation $R = \frac{Vb}{V - Va}$ that the determination of the specific volumes of saturated vapours cannot be nearly so accurate as those of the liquids. For a given volume of vapour Vb, the difference between V and Va increases with rise of temperature, since the vapour becomes denser, and, therefore, in any series of determinations, the results are more reliable at high than at low temperatures.

Again, at a given temperature the differences between the true and apparent volumes of liquid vary directly with the volume of saturated vapour, and, therefore, most weight should be given to those series in which the volume of vapour is largest. From this point of view, Series II should be the most accurate in the case of carbon tetrachloride, while the third series should receive greater weight than the first. With stannic chloride, the arrangement of the series in order of accuracy is III, IV, II, I.

The critical volumes of carbon tetrachloride and stannic chloride have not been determined directly, but the following approximate values have been arrived at by a comparison of the molecular volumes of these substances with those of fluorobenzene by a method described in a paper shortly to be read before the Physical Society.

	Critical volume of a gram.	Critical molecular volume.
Carbon tetrachloride	1·53	235
Stannic chloride	1·16	301

It is quite clear that no such simple relations hold good between carbon tetrachloride and stannic chloride, as between the halogen derivatives of benzene, but from the boiling points and other properties of the chlorides of the tetrad group of elements, it has been inferred that they should be subdivided into two groups, thus:—

	B. p.		B. p.
Carbon tetrachloride..	76·74°		
		Silicon tetrachloride....	57·57°
Titanium tetrachloride	136·40		
		Germanium tetrachloride	86·00
Zirconium tetrachloride (very high)			
		Stannic chloride	114·10

The chlorides of the carbon group of elements possess higher boiling points than do those of the silicon group nearest to them in the series.

I hope to be able before long to communicate the results of determinations of the vapour pressures and molecular volumes of silicon tetrachloride and titanium tetrachloride.

LXXXII.—*On the Freezing Points of Triple Alloys of Gold, Cadmium, and Tin.*

By C. T. Heycock, M.A., and F. H. Neville, M.A.

In previous communications to the Society (Proc., No. 65, p. 41; Trans., 1889, **55**, 667; 1890, **57**, 376) we described experiments on the freezing points of alloys of two metals. In the course of subsequent work, of which a brief abstract has been published (Proc., No. 88, p. 158), we found that when several metals are in solution together their effects in lowering the freezing point of the solvent metal were independent of each other's presence, so long as the solution remained dilute. The present communication contains the results of experiments on more concentrated solutions, containing gold and cadmium, dissolved in tin. In these cases, as will be seen, the phenomena are of an entirely different character, and there is no simple relation between the quantity of foreign metal present and the fall of the freezing point.

The experiments were made as described in the paper on tin solutions (Trans., 1890, 57, 376), in the axis of thick iron cylinders, except that to ensure a greater accuracy the thermometers were graduated* every 10 mm. against a platinum thermometer, as described by Griffiths (*B.A. Reports*, 1890), and the results, mapped on a large scale, were used for determining temperatures.

In order, as far as possible, to protect the long stem of the thermometer from currents of heated air, the top of the iron block was covered with a plate of asbestos, 14 inches square. The same precaution had been previously taken when determining the fixed points on the thermometer. When working with concentrated solutions, we found it necessary to drop in small nuclei of previously solidified alloy, in order to prevent too great surfusion; without this precaution we were unable to obtain concordant results.

The course of an experiment was as follows:—300 grams of pure tin was placed in the block, and the freezing point taken several times with great care; weighed quantities of one of the foreign metals were then added in successive doses, until the requisite quantity was present, the freezing point being determined after each addition, vigorous automatic stirring being maintained. To this solution, the second foreign metal was added in the same way. Since both gold and cadmium dissolve in tin with great ease, it was found sufficient to drop the weighed quantities of gold and cadmium directly into the block. The results were mapped on a large scale, by marking off the number of atoms of foreign metal present per 100 atoms of tin, horizontally, from left to right, and the temperatures of the freezing point vertically downwards. The curves thus obtained, showing the connection between the composition of the alloy and the freezing temperature, are reproduced on a small scale with the present paper. In the tables which accompany this paper, the actual experimental results are given.

The curves obtained in this way present certain similarities which allow of their being classified into three types:—Type I, when the first metal (Au or Cd) is not present to the extent of more than 3 atoms per 100 atoms of tin.*

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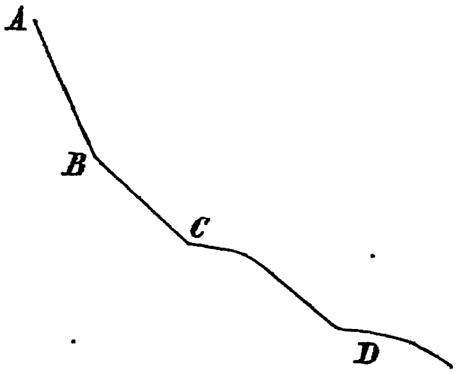
* We were greatly assisted in the work of graduating the thermometer by Mr. G. M. Clark, of Sidney College, and also by Mr. E. H. Griffiths, and we wish here to record our best thanks to them.

Type II, when the first metal is present to the extent of more than 3 atoms, but does not saturate the liquid.

Type III, when more of the first metal has been added to the tin than is required to produce the *eutectic* or saturated alloy.

Curves of Type I may be diagrammatically represented thus—

TYPE I.



Vertical distances are falls in temperature; horizontal distances, atoms of Au or Cd.

AB = fall caused by gold.
BCD = „ „ cadmium.

Curves of this type have only been produced by adding gold first, and then cadmium. It will be seen that each addition of cadmium produces a further effect. but the magnitude of this effect varies very much from place to place, being a minimum, or, perhaps, *nil*, at the points of inflexion. (See Plate 1, p. 966, and Tables I and II.)

The 3-atom gold curve, Table III, and Plate 1, shows the transition from a curve of Type I to one of Type II.

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* In future, we propose to speak simply of the *number of atoms* of foreign metal present. By this we mean the number of foreign atoms per 100 atoms of tin.

TABLE I.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·42)	—	—	*
10·026	—	10·026	225·73	2·0	5·69	
Now added Cadmium.						
—	1·374	1·374	224·68	0·483	6·74	
—	1·539	2·913	223·66	1·024	7·76	
—	3·790	6·703	220·94	2·355	10·48	No infusible residue.

TABLE II.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·42)	—	—	
1·650	—	1·650	230·55	0·3292	0·87	
Now added Cadmium.						
—	0·308	0·308	230·27	0·1082	1·15	Nuclei of alloy used in all these experiments.
—	0·277	0·585	230·05	0·2055	1·37	
—	0·308	0·893	229·78	0·3137	1·64	
—	0·2782	1·171	229·55	0·4114	1·87	
—	0·3980	1·569	229·23	0·5512	2·19	
—	0·3890	1·958	228·91	0·6878	2·51	
—	0·902	2·86	228·17	1·0045	3·25	
—	1·238	4·098	227·11	1·439	4·31	
Now added Gold.						
4·737	—	6·387	224·72	0·9451	6·70	
3·639	—	10·026	222·77	2·00	8·65	

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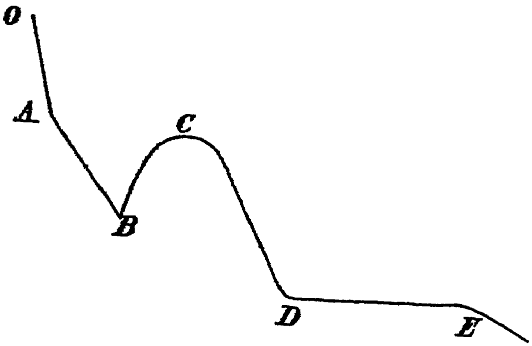
* As a general rule, each series of experiments was carried out with the thermometer known to us as Hicks' No. 10. When the temperature fell below the range of this thermometer, we used Hicks' No. 9.

TABLE II—*continued.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
		Now added Cadmium.				
—	3·880	7·978	220·11	2·802	11·31	
—	1·535	9·513	219·01	3·341	12·41	
—	1·449	10·962	218·1	3·85	13·32	
—	1·424	12·386	217·33	4·35	14·09	
—	1·102	13·488	216·76	4·73	14·66	
—	1·375	14·863	216·04	5·220	15·38	
—	1·796	16·659	215·21	5·851	16·21	
—	3·449	20·108	214·41	7·062	17·01	
—	1·816	21·924	213·87	7·70	17·55	
—	1·109	23·033	213·41	8·09	18·01	
—	2·135	25·168	212·45	8·839	18·97	Changed to Hicks' No. 9.
—	2·414	27·582	211·48	9·687	19·94	
—	2·831	30·413	210·73	10·681	20·69	
—	2·843	33·256	210·42	11·679	21·00	
—	2·712	35·968	210·24	12·631	21·18	
—	3·062	39·03	209·72	13·706	21·70	
—	3·168	42·198	208·91	14·82	22·51	
—	4·143	46·341	207·76	16·27	23·66	
—	7·915	54·256	205·2	19·05	26·22	

Curves of the second type, when the first metal is present in quantity insufficient to saturate the liquid, are represented by the broken line OABCDE, where the line OA corresponds to the fall caused by the first metal, say gold, and the remainder to the effect of adding cadmium. The point B is certainly an angle, and a precipitate is

TYPE II.



formed after this point is reached. C is a rounded summit. D appears to be an angle, or a very sharp curve, whilst at E the change of curvature is gradual.

Here it will be seen (Plate 2, p. 966) that the summit C, and in those cases in which gold is the first metal added, the flat DE, always occur at the same temperature, whatever the amount of gold or cadmium initially added. *The summit C invariably reached when the number of gold atoms is equal to the number of cadmium atoms*, in other words, the minimum fall in the freezing point of tin is produced with this ratio of gold to cadmium. Thus, for example, the summit C has been reached with 4 atoms of gold and 4 atoms of cadmium, 5 atoms of gold and 5 atoms of cadmium, 9 atoms of gold and 9 atoms of cadmium per 100 atoms of tin, and all these alloys are *isotectic.**

TABLE III.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·44)	—	—	
15·07	—	15·07	222 77	3·007	8·69	
Now added Cadmium.						
—	1·011	1·011	222·14	0·355	9·30	Same reading with nuclei of either Sn or alloy.
—	1·144	2·155	221·38	0·757	10·06	
—	1·703	3·858	220·28	1·355	11·16	
—	1·463	5·321	219·37	1·869	12·07	
—	1·512	6·833	218·3	2·400	13·14	
—	1·669	8·502	217·26	2·986	14·18	
—	1·561	10·063	216·93	3·534	14·51	
—	1·499	11·562	217·2	4·061	14·24	
—	1·209	12 772	217·06	4·485	14·38	
—	1·658	14·430	216·86	5·068	14·58	
—	2·528	16·958	216·37	5·956	15·07	
—	3·025	19·983	215·55	7·018	15·89	
—	3·269	23·25	214·38	8·166	17·06	
—	2·845	26·097	213·35	9·165	18·09	
—	3·720	29·817	211·77	10·47	19·67	Changed thermometer.
—	3·990	33·807	210·69	11·872	20·75	
—	3·183	36·99	210·65	12·99	20·79	
—	3·366	40·35	210·51	14·172	20·93	
—	4·161	44·517	210·46	15·633	20·98	
—	6·242	50·76	209 08	17·825	22·36	
—	8·845	59·604	206·32	20·931	25·12	

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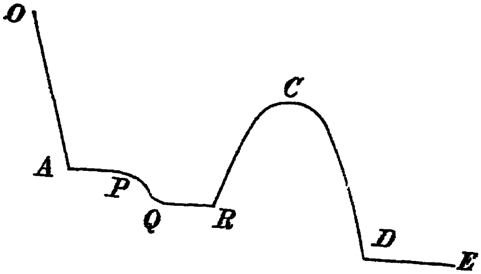
* Isotectic substances are those which melt at the same temperature.

TABLE IV.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·42)	—	—	
2·087	—	2·087	230·22	0·4164	1·20	
11·99	—	14·077	223·41	2·809	8·01	
5·848	—	19·925	219·95	3·976	11·47	
Now added Cadmium.						
—	0·951	0·951	219·37	0·334	12·05	
—	1·015	1·966	218·66	0·691	12·76	
—	1·157	3·123	218·0	1·097	13·42	
—	1·062	4·185	217·28	1·47	14·14	
—	1·022	5·206	216·76	1·83	14·66	
—	1·265	6·473	217·01	2·274	14·41	
—	1·004	7·477	217·17	2·625	14·25	
—	1·362	8·839	217·32	3·104	14·10	
—	1·720	10·559	217·41	3·709	14·01	
—	0·912	11·471	217·54	4·032	13·88	
—	1·242	12·713	217·37	4·469	14·05	
—	1·477	14·19	217·1	4·988	14·32	
—	1·438	15·628	216·93	5·493	14·49	
—	1·404	17·032	216·67	5·986	14·75	
—	1·416	18·448	216·34	6·483	15·08	
—	1·37	19·818	215·95	6·963	15·47	
—	3·220	23·038	214·87	8·095	16·55	
—	3·038	26·076	213·78	9·162	17·64	
—	3·168	29·244	212·5	10·275	18·92	
—	3·715	32·96	210·9	11·58	20·52	
—	3·175	36·134	210·66	12·695	20·76	
—	3·027	39·161	210·56	13·76	20·86	
—	3·595	42·756	210·19	15·02	21·23	
—	1·757	44·513	210·72	15·638	20·70	
—	10·476	54·989	209·73	19·318	21·69	
—	5·112	60·101	208·43	21·114	22·99	
—	5·30	65·401	206·78	22·976	24·64	
—	5·15	70·551	204·95	24·785	26·47	
—	5·315	75·866	203·08	26·652	28·34	
—	7·130	82·996	200·48	29·153	30·94	

Curves of the third type are obtained when more gold has been added than the amount required to saturate the tin. Here the slope OA and the flat AP are due to the gold. PQ shows the effect of the first quantities of cadmium, the fall from P to Q being independent of the amount of gold present; this is true for all the curves of Type III. Directly the point Q is reached a precipitate begins to separate out in the block and remains to the end of the experiment. The part QR is of different lengths in different curves; it is probable, however, that the horizontal distance PR equals AP, in other words, that the cadmium begins to produce a rise when as many atoms of it are present as there are atoms of gold in excess of the saturation amount.

TYPE III.



From R onwards the curve closely resembles Type II, the summit C of least effect, and the flat DE occurring at identical temperatures in the two classes of curves; moreover, C is reached when the number of atoms of cadmium is equal to the number of atoms of gold.

TABLE V.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·55)	—	—	
25·06	—	25·06	217·12	5·0	14·43	
		Now added Cadmium.				
—	1·045	1·045	216·5	0·367	15·05	
—	1·14	2·185	215·88	0·767	15·67	
—	1·30	3·485	215·16	1·224	16·39	
—	1·025	4·51	214·64	1·58	16·91	
—	0·5585	5·068	215·24	1·78	16·31	
—	0·7445	5·813	215·7	2·041	15·85	
—	1·46	7·273	216·39	2·554	15·16	
—	1·315	8·588	216·84	3·015	14·71	
—	1·174	9·762	217·15	3·428	14·40	
—	1·364	11·126	217·42	3·907	14·13	
—	0·936	12·062	217·58	4·235	13·97	
—	0·897	12·959	217·64	4·55	13·91	
—	0·753	13·712	217·69	4·82	13·86	
—	0·720	14·432	217·69	5·07	13·86	

TABLE VI.—300 *grams of Tin taken as a Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·41)	—	—	
1·249	—	1·249	230·66	0·249	0·75	
1·610	—	2·858	229·78	0·57	1·63	
4·6125	—	7·471	227·14	1·491	4·27	
10·3785	—	17·850	221·1	3·561	10·31	
8·0565	—	25·907	216·37	5·17	15·04	
5·314	—	31·22	213·51	6·23	17·9	Changed thermometer to Hicks' No. 9.
1·925	—	33·15	213·36	6·614	18·05	
		Now added Cadmium.				
—	1·0465	1·0465	213·15	0·3675	18·26	
—	3·122	4·1685	212·64	1·464	18·77	
—	2·713	6·881	212·64	2·417	18·77	Hicks' thermo. No. 10.
—	3·101	9·982	215·71	3·506	15·7	
—	3·063	13·045	216·81	4·581	14·6	
—	3·1475	16·193	217·48	5·686	13·93	
—	2·63	18·823	217·65	6·61	13·76	
—	2·921	21·744	217·28	7·636	14·13	
—	2·58	24·324	216·93	8·542	14·48	Raised to high temp. for 1 hour.
—	2·576	26·90	216·29	9·447	15·12	
—	3·09	29·99	215·3	10·532	16·11	
—	3·89	33·88	213·84	11·898	17·57	
—	3·58	37·47	212·33	13·155	19·08	
—	11·772	49·232	210·60	17·29	20·81	Changed to Hicks' No. 9.
—	3·826	53·058	210·6	18·633	20·81	
—	4·643	57·70	210·59	20·26	20·82	
—	10·065	67·766	210·03	23·799	21·38	

TABLE VII.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·51)	—	—	
30·57	—	30·57	213·75	6·099	17·76	
1·031	—	31·601	213·55	6·305	17·96	
4·661	—	36·262	213·49	7·235	18·02	
3·834	—	40·096	213·46	8·00	18·05	
5·012	—	45·108	213·45	9·00	18·06	Hicks' No. 9.

TABLE VII—*continued.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
		Now added Cadmium.				
—	1·077	1·077	213·0	0·378	18·51	
—	1·298	2 375	212·68	0·834	18·83	
—	1·231	3·606	212·46	1·266	19·05	
—	1·446	5·05	212·44	1·775	19·07	
—	1·177	6·229	212·45	2·158	19·06	
—	1·466	7·695	212 55	2·703	18·96	
—	1·367	9·062	212·55	3·183	18·96	
—	1·412	10·474	212·72	3·679	18·79	Changed to Hicks' No. 10.
—	1·65	12·124	213·33	4·258	18·18	
—	1·998	14·122	214·54	4·960	16·97	
—	1·818	15·940	215·5	5·599	16·01	
—	1·525	17·465	216·19	6·134	15·32	
—	1·585	19·050	216·83	6·691	14·68	
—	1·945	20·995	217·36	7 374	14·15	A large quantity of precipitate at bottom of block.
—	1·374	22·369	217·59	7·856	13·92	
—	1·648	24·02	217·7	8·436	13·81	
—	1·520	25·537	217·68	8·97	13·83	
—	1·506	27·043	217·52	9·498	13·99	
—	2·208	29·251	217·17	10·274	14·34	
—	3·806	33·06	216·3	11·611	15·21	
—	3·285	36·34	215·2	12·765	16·31	
—	4·853	41·195	213·33	14·47	18·18	
—	3·947	45·14	211·4	15·851	20·11	Thermo. Hicks' No. 9.
—	1·424	46·566	210·75	16·354	20·76	
—	1·352	47·92	210·6	16·829	20·91	
—	1·579	49·497	210·66	17·384	20·85	
—	1·714	51·211	210·63	17·986	20·88	
—	1·762	52·973	210·6	18·61	20·91	
—	2·01	54·983	210·6	19·311	20·91	
—	2·095	57·08	210·6	20·05	20·91	
—	1·650	58·73	210·6	20·63	20·91	
—	1·062	59·79	210·6	21·0	20·91	
—	1·71	61·50	210·51	21·6	21·00	
—	1·761	63·26	210·66	22·22	20·85	
—	2·744	66·0	210·55	23·18	20·96	
—	2·959	68·96	210·46	24·22	21·05	
—	2·666	71·63	210·44	25·156	21·07	
—	1·850	73·48	210·43	25·81	21·08	
—	2·286	75·764	210·03	26·61	21·48	

TABLE VIII.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	tin (231 57)	—	—	
25·06	—	25·06	217·23	5·0	14·34	
5·012	—	30·072	214·29	6·0	17·28	
0·802	—	30·874	213·77	6·16	17·80	
0·511	—	31·385	213·6	6·262	17·97	
2·232	—	33·617	213·57	6·707	18·00	
5·048	—	38·665	213·53	7·714	18·04	
8·932	—	47·597	213·53	9·497	18·04	
7·535	—	55·132	213·52	11·00	18·05	
		Now added Cadmium.				
—	0·3585	0·3585	213·47	0·1259	18·10	
—	0·664	1·0225	213·43	0·359	18·14	
—	0·530	1·5525	213·32	0·5454	18·25	
—	0·752	2·3045	213·12	0·8095	18·45	
—	0·498	2·8025	213·01	0·9844	18·56	
—	0·575	3·3775	212·9	1·1864	18·67	
—	0·480	3·858	212·86	1·355	18·71	
—	0·770	4·628	212·81	1·625	18·76	
—	1·006	5·634	212·78	1·978	18·79	
—	1·465	7·099	212·8	2·493	18·77	
—	6·638	13·737	212·86	4·8246	18·71	
—	6·558	20·295	215·66	7·128	15·91	
—	2·683	22·979	216·88	8·0713	14·69	
—	2·028	25·006	217·49	8·7835	14·08	

TABLE IX.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	tin (231·51)	—	—	
—	2·694	2·694	229·2	0·946	2·31	
—	3·048	5·742	226·71	2·017	4·80	
—	2·454	8·196	224·75	2·878	6·76	
—	3·194	11·390	222·45	4·0	9·06	

TABLE IX—*continued.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C D.	Remarks.
Now added Gold.						
1·1295	—	1·1295	221·95	0·2253	9·56	
0·99	—	2·1195	221·53	0·4228	9·98	
1·059	—	3·1785	221·05	0·634	10·46	
1·011	—	4·1895	220·59	0·8358	10·92	
1·122	—	5·3115	220·12	1·0596	11·39	
1·018	—	6·329	219·62	1·263	11·89	
1·047	—	7·376	219·17	1·472	12·34	
1·008	—	8·384	218·71	1·673	12·8	
1·01	—	9·394	218·26	1·874	13·25	
1·01	—	10·403	217·77	2·075	13·74	
1·005	—	11·481	217·36	2·276	14·15	
1·082	—	12·491	216·88	2·492	14·63	
1·003	—	13·493	217·11	2·692	14·4	
1·001	—	14·495	217·27	2·892	14·24	
1·002	—	15·496	217·38	3·09	14·13	
1·013	—	16·509	217·49	3·294	14·02	
1·001	—	17·511	217·55	3·493	13·96	
1·085	—	18·595	217·59	3·71	13·92	
1·008	—	19·603	217·69	3·911	13·82	
1·044	—	20·647	217·69	4·12	13·82	
2·0	—	22·647	217·65	4·518	13·86	
3·015	—	25·662	217·38	5·120	14·13	
4·045	—	29·707	216·97	5·927	14·57	
2·763	—	32·471	216·62	6·478	14·89	
2·035	—	34·506	216·16	6·884	15·35	
2·299	—	36·805	215·54	7·343	15·97	
2·51	—	39·32	214·79	7·843	16·72	
2·55	—	41·86	213·99	8·352	17·52	
2·662	—	44·53	212·77*	8·383	18·74	
2·591	—	47·117	212·77	9·4	18·74	
2·795	—	49·91	212·77	9·96	18·74	
2·706	—	52·62	212·77	10·498	18·74	
2·601	—	55·22	212·77*	11·02	18·74	
2·555	—	57·774	212·77	11·526	18·74	
2·096	—	59·87	212·77	11·944	18·74	
2·6	—	62·47	212·77	—	18·74	
2·586	—	65·056	212·77*	—	18·74	
2·428	—	67·484	212·77	—	18·74	
2·596	—	70·078	212·77	13·98	18·74	
Now added Cadmium.						
—	14·859	26·25	214·16	9·217	17·35	

* Fluctuations did not exceed 0·03°.

TABLE X.—300 *grams of Tin taken as Solvent.*

Grams of Au added in succession.	Grams of Cd added in succession.	Total weight of Au or Cd added.	Freezing point of solution.	Atoms of Au or Cd per 100 atoms of tin.	Falls in ° C. D.	Remarks.
—	—	—	(tin 231·58)	—	—	
—	3·726	3·726	228·37	1·309	3·21	
—	3·932	7·658	225·23	2·69	6·35	
—	3·668	11·326	222·53	3·975	9·05	
—	8·609	19·935	217·79*	7·0	13·79	
			Now added Gold.			
1·2685	—	1·2685	217·32*	0·2531	14·26	
1·0895	—	2·358	216·7*	0·47	14·88	
1·5655	—	3·9235	216·07	0·783	15·51	
1·333	—	5·3065	215·55	1·059	16·03	
1·0645	—	6·371	215·18	1·271	16·40	
2·251	—	8·622	214·38	1·72	17·20	
1·112	—	9·734	214·59	1·942	16·99	
1·486	—	11·22	214·92	2·239	16·66	
1·126	—	12·346	215·13	2·461	16·45	
1·215	—	13·561	215·43	2·703	16·15	
6·488	—	20·05	216·44	4·0	15·14	

In order to gain some insight into the changes that have gone on in the blocks, analyses were made of the liquid portion and the precipitate at various points on the curves of Types II and III.

The collection of pure samples of the liquid and precipitate presents considerable difficulty, for the composition of the liquid is affected by the change of solubility of the precipitate with the temperature, whilst the composition of the precipitate is affected by the mother liquor adhering to it. After several trials, the following plan for collecting the liquid and precipitate was found to yield fair results:—At the termination of an experiment the temperature of the block or crucible was kept as nearly as possible stationary, a few degrees above the freezing point of the alloy, rapid stirring being maintained for a quarter of an hour. The thermometer was then withdrawn, the stirrer stopped, and the precipitate allowed to subside for two or three minutes. Some of the supernatant liquid was then sucked up by means of a very fine pointed pipette, which had been previously heated to prevent the alloy solidifying. Owing to the fine point of the pipette and the time allowed for the precipitate to subside, the mechanical introduction of

* Some experimental error which apparently corrects itself later on.

the precipitate, along with the fluid part, was to a large extent avoided. After the alloy had solidified, the pipette was broken, and the cylinder of metal was cleaned from adhering paraffin,* remelted at as low a temperature as possible, and afterwards granulated by throwing into water.

To obtain the precipitate, the residue in the block, after withdrawing part of the fluid, was poured into an iron-wire gauze bag, placed in a bath of molten paraffin, at a temperature above the melting point of the fluid part of the alloy; by repeatedly raising the bag out, and tapping it against the iron block, the precipitate could be obtained fairly free from mother liquor. The precipitate crystallised in well-marked hexagonal plates. The analysis of the fluid part, or mother liquor, and the precipitate, was made as follows :—

A weighed quantity of the alloy, from 2 to 3 grams, was placed in a beaker, and treated with pure, concentrated hydrochloric acid, and digested for several hours on a sand-bath, the liquid being decanted off, and fresh portions of hydrochloric acid added from time to time. The gold left behind after the solution of the cadmium and tin, was collected, washed, and weighed.

The separation of the cadmium and tin contained in the wash waters was effected by a modification of Löwenthal's method. The mixture of stannous and cadmium chlorides was oxidised with bromine, and the liquid neutralised with ammonia until a precipitate just formed. The solution was then diluted, warmed upon a sand-bath, and a concentrated solution of a mixture of sodium sulphate and ammonium nitrate† added; the whole was then left for some hours on the sand-bath, and, after cooling, the precipitate of hydrated tin dioxide was collected and washed on a filter pump. In a few cases this precipitate was repeatedly ignited and weighed in order to estimate the tin directly; but usually the tin was determined by difference.

After the separation of the tin, the cadmium in the filtrate was precipitated as sulphide by sulphuretted hydrogen. The cadmium sulphide was filtered and washed to free it from ammonium and sodium salts, and then dissolved off the filter by hot dilute hydrochloric acid. After filtering, the pure solution of cadmium chloride was precipitated at the boiling point with sodium carbonate. The precipitated cadmium carbonate was collected on a filter, washed, dried, and transferred, as far as possible, to a porcelain crucible; the filter paper, with adhering traces of cadmium oxide, was burnt after previous moistening with ammonium nitrate. The cadmium carbonate was ignited over the blowpipe and weighed as cadmium oxide. The results are almost certainly too low,[*] owing to a slight reduction of the oxide and volatilisation of the cadmium. The purity of the ignited cadmium oxide was ascertained by dissolving it in warm dilute nitric acid, any residue left being collected and weighed as tin dioxide.[†] The cadmium results have in several instances been confirmed by simply treating weighed quantities of the alloy with nitric acid, evaporating to dryness, and igniting the residue. The cadmium oxide was dissolved out with dilute nitric acid, precipitated as carbonate, and weighed as oxide; the results of this control gave in all cases 0·2—0·3 per cent. more cadmium than the previous method.

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* The whole of our freezing-point experiments were conducted under a layer of molten paraffin.

† We found the mixture of Na_2SO_4 and NH_4NO_3 act much more rapidly than NH_4NO_3 alone, as recommended by Löwenthal.

For the convenience of description and classification, the results in Table XI (pp. 951, 952) are not given in chronological order.

On examining the numbers in the tables, it will be seen that, although the gold and cadmium have been dissolved in tin in very various proportions, the ratio of gold atoms to cadmium atoms are as 1 : 1 in the precipitate, or, as analysis shows (with the exception of the results of Table VI), more nearly $Au_{1\cdot18}Cd$. With regard to the large quantity of tin present in the precipitates, part, no doubt, is due to adhering mother liquor;[‡] but we have strong reason for believing that another part enters as an essential constituent of the compound. We have made several attempts to clear up this point by endeavouring to reduce, as far as possible, the adhering tin. For this purpose, experiments were made on the precipitate collected after the results given in Table IX. Analysis of this precipitate have as mean results Au 31·96 per cent., Cd 14·62 per cent.

A solid steel piston, about half an inch in diameter, was turned to fit a hole in a steel block or cylinder about 3 inches deep. The bottom of this cylinder was perforated by a number of fine holes over which was placed a disc of fine iron-wire gauze. This cylinder was placed in the axis of one of our large blocks and heated to the necessary temperature. From 2 to 3 grams of the precipitate were then placed in the cylinder and kept at a temperature nearly 100° above the melting point of the liquid part of the alloy; the piston was then hammered in with a mallet, when a considerable portion of

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[*] Fresenius (English translation, 1876), 7th ed., p. 266, says that the "results of estimating cadmium as oxide are generally a little too low."

[†] The frequent presence of a little SnO_2 in this precipitate confirms the work of previous observers, that all attempts to precipitate Sn as hydrated oxide in presence of hydrochloric acid are only partially successful.

[‡] This tin would doubtless be accompanied by corresponding quantities of gold and cadmium.

TABLE XI.—*Analyses.*

Original composition of mixture in block.				Composition of fluid part.			Composition of the insoluble precipitate.			
Reference to tables.	Au.	Cd.	Sn.	Au p.c.	Cd p.c.	Sn p.c.	Au p.c.	Cd p.c.	Sn p.c.	Atoms Au : atoms Cd in precipitate.
II.	2 atoms	19·05 atoms	100 atoms	—	—	—	—	—	—	
	8·3 p.c.	16·9 p.c.	74·8 p.c.	2·15	—	—	13·7	—	—	
III.	3 atoms	20·9 atoms	100 atoms	—	—	—	—	—	—	
	—	—	—	1·96	—	—	13·5	—	—	
IV	3·076 atoms	29·15 atoms	100 atoms	—	—	—	28·5	—	—	
	4·78 p.c.	20·63 p.c.	74·6 p.c.	1·4	—	—	18·8	—	—	
	—	—	—	1·5	—	—	28·5	—	—	
V.	5 atoms	5·06 atoms	100 atoms	4·98	2·51	—	23·99	11·82	—	$Au_{1·15}Cd$.
	7·38 p.c.	4·25 p.c.	88·37 p.c.	4·92	—	—	22·89	—	—	
	—	—	—	5·1	—	—	22·01	11·4	65·8	$Au_{1·09}Cd$.
	—	—	—	5·13	2·4	—	—	—	—	
VI	6·61 atoms	23·8 atoms	100 atoms	3·66	—	—	18·4	—	—	
	8·27 p.c.	16·9 p.c.	74·8 p.c.	3·52	—	—	28·02	—	—	
	—	—	—	—	—	—	20·31	—	—	

TABLE XI—*continued*.

Reference to tables.	Original composition of mixture in block.			Composition of fluid part.			Composition of the insoluble precipitate.			
	Au.	Cd.	Sn.	Au p.c.	Cd p.c.	Sn p.c.	Au p.c.	Cd p.c.	Sn p.c.	Atoms Au : atoms Cd in precipitate.
VII..........	11 atoms	8·78 atoms	100 atoms	5·81	—	—	29·16*	13·83	56·67	$Au_{1·2}Cd$.
	11·5 p.c.	6·58 p.c.	78·9 p.c.	5·93	—	—	30·57	11·73	—	$Au_{1·18}Cd$.
	—	—	—	5·73	1·83	—	30·45	—	—	
	—	—	—	5·74	—	—	—	—	—	
	—	—	—	5·8	2·29	—	—	—	—	
	—	—	—	5·72	2·12	—	—	—	—	
VIII..........	9 atoms	26·6 atoms	100 atoms	8·51	—	—	23·54	29·27	—	$AuCd_{2·18}$ †
	10·72 p.c.	18 p.c.	71·28 p.c.	3·38	9·86	86·3	—	—	—	
	—	—	—	—	—	—	34·01‡	43·97	-	$AuCd_{2·3}$.
IX..........	—	—	—	8·68	—	—	31·6	15·0	—	$Au_{1·19}Cd$.
	—	—	—	8·7	1·7	—	31·7	11·1	53·6	$Au_{1·28}Cd$.
	13·98 atoms	0·217 atoms	100 atoms	8·71	1·56	—	32 6	14 76	52 6	$Au_{1·2}Cd$.
	17·68 p.c.	0·62 p.c.	7·57 p.c.	8·75	1·38	89·07	—	—	—	
	—	—	—	8·57	1·52	88·8	39·02‡	18·81	—	$Au_{1·18}Cd$.
	—	—	—	8·81	1·3	—	10·67‡	20·18	—	$Au_{1·11}Cd$.
X..........	—	—	—	3·46	4·48	91·61	21·96*	14·6	59·2	$Au_{0·972}Cd$.
	4 atoms	7 atoms	100 atoms	3·58	4·96	90 02	13·74	8·74	77·01	$Au_{0·894}Cd$.
	5 86 p.c.	5·89 p.c.	88 24 p.c.	—	—	—	17·5	11·68	—	$Au_{0·859}Cd$.

* Sample of precipitate collected off thermometer stem. † This point is on the flat DE. ‡ Hammered disc of precipitate.

the fluid part was expelled, the residue being left as a thin wad or disc which could easily be driven out of the cylinder.

Two experiments were made on the precipitate obtained in Table IX.

Disc I, hammered at 280°, weighed 3·3815 grams.

Analysis gave—

39·02	per cent.	Au,
18·81	„	Cd,
42·17	„	Sn (by difference).

This gives the formula $Au_{1\cdot 18}CdSn_{2\cdot 13}$.

Disc II, hammered above 300°, weighed 1·3425 grams.

Analysis gave—

40·67	per cent.	Au,
20·19	„	Cd,
39·14	„	Sn (by difference).

This gives the formula $Au_{1\cdot 14}CdSn_{1\cdot 84}$

Before hammering, the precipitate gave as the mean of three concordant experiments, Au 31·94, Cd 14·62, Sn 53·44. Theory requires for the body Sn_2AuCd

Au............	36·2	per cent.
Cd............	20·5	„
Sn............	43·3	„

It will be seen that whilst the percentage of tin was reduced in the one case by 11·3, and in the other by 14·3, the ratio of the Au to the Cd remained almost the same as before the experiment. The foregoing precipitate was produced during an experiment which was concluded just before the angle D of the final flat was reached (see Plate 3).

From the above experiments we conclude that the gold and cadmium unite atom for atom, for the following reasons:—

(*a.*) 12 analyses of five different precipitates give the mean ratio $Au_{1\cdot 1}Cd$.

(*b.*) This ratio remains the same, although the proportions in which the gold and cadmium were dissolved in the tin varied from 5·86 atoms Au for 5·89 atoms Cd to 14·5 atoms of Au for 6·2 atoms of Cd.

(*c.*) The ratio Au : Cd cannot be disturbed by liquation.

(*d.*) The minimum lowering of the freezing point of the tin is produced when the gold and cadmium are present atom for atom.

(*e.*) From solutions containing low percentages of gold and cadmium, we obtain precipitates rich in these metals.

Special interest attaches to the 3rd flat DE in the curves on Plate 3 (p. 966) of Table VII.

Here in one case the gold and cadmium had been dissolved in the ratio 9Au : 26·6Cd.

Analysis of the precipitate gave 23·54 per cent. Au,
29·27 „ Cd,

corresponding to the formula AuCd$_{2\cdot19}$.

On liquating and hammering a portion, as previously described. the following results were obtained :—

Disc hammered at 310° weighed 2·503 grams.

Analysis gave—

34·04 per cent. Au,
43·97 „ Cd,
21·99 „ Sn (by difference),

corresponding to the formula AuCd$_{2\cdot3}$Sn$_{1\cdot1}$.

Hence we conclude that two compounds are formed. Up to the angle D (Curves Types II and III, Plates 2 and 3) the compound formed is AuCdSn$_2$; on the further addition of cadmium, one of the atoms of tin is displaced, and the compound AuCd$_2$Sn is formed.

The discussion of the results of analysis of the fluid part of the alloy is given at the end of the paper, but it will be sufficient to point out here that if the tin is rich in gold it is poor in cadmium, and *vice versâ.*

Interpretation of above Results.

In attempting to interpret these curves in a more precise manner, we must start from the principle that, when any single metal is in solution in tin, the fall in the freezing point is a measure of the number of molecular weights of this metal present. Our previous experiments have made it probable that the molecule of a metal when dissolved in tin consists of 1 atom. If, therefore, gold and cadmium, when dissolved together in tin, produce a total fall which is less than the sum of the falls that each alone would produce, the difference is probably produced by the action of the gold and the cadmium on each other.

A certain influence, which we may call mechanical or thermodynamical, is exerted by each dissolved metal on the osmotic pressure of any other dissolved metal, and therefore on the fall in the freezing point of the solvent caused by the latter. Moreover, gold probably increases the apparent effect of another dissolved metal by combining with some of the tin, and so practically decreasing the amount of the solvent, and making the solution of the other metal more concentrated. But these are minor causes, and would not produce the phenomena recorded in the curves.

The main cause is probably the combination of the gold and cadmium atoms to form molecules. It is clear that this would cause a rapid decrease in the total fall even if everything remained in solution; but our filtration experiments above the freezing point of tin, when large quantities of precipitate were formed, seem to prove that the new body is very sparingly soluble in tin. Hence, when gold and cadmium are brought together in solution in tin, a considerable quantity of these metals is removed from solution, and the total fall becomes much less than the sum of the separate falls.

The analyses of the crystalline precipitate, and to some extent a study of the part from A to R in curves of Type III (p. 943), point to the conclusion that 1 atom of gold combines with 1 atom of cadmium, so that as far as these metals are concerned, the molecule of the compound formed has the formula Au_nCd_n. It will be seen, when we consider the equations of equilibrium, that the occurrence of the summits C, corresponding to a minimum fall, at the moment when an equal number of atoms of gold and cadmium have been added, strongly supports the formula Au_nCd_n.

It is very probable that the tin also reacts chemically with the other two metals, and may be an important constituent of the molecule of the compound; but the tin, from its large amount compared with the amounts of the gold and cadmium, must have a practically constant active mass, and hence it does not seem indispensable to take it into consideration in discussing the equilibrium.

We shall, therefore, in what follows assume that a portion of the gold and cadmium combine to form molecules of the type Au_nCd_n, while the remainder of the two metals is present in the form of monatomic molecules.

Let a and c be the total numbers of gold and cadmium atoms for every 100 atoms of tin *present in the vessel*, x and y the number of monatomic molecules of these metals present, and z the number of molecules of the body Au_nCd_n that has been formed. Then it is obvious that

$$a = x + nz; \; c = y + nz.$$

Let us consider the progress of the changes during the experiments recorded by a curve of the Type II. As we start from the state A of a pure solution of gold in tin, and advance towards B by adding cadmium, we have at each step a state of equilibrium between x atoms of gold, y atoms of cadmium, and z molecules of Au_nCd_n.

It seems probable that up to the point B the compound all remains in solution, but that B corresponds to the saturation of the tin by the compound. Indeed, soon after B is past, we can detect a precipitate at the bottom of the block.

As the fluctuations of temperature along any one of the curves only amount to about 20°, a small fraction of the absolute temperature of 500°, we propose in the equation of equilibrium to ignore these changes and regard the equilibrium as isothermal.

The principle of Guldberg and Waage then leads to the equation

$$\frac{xy}{\sqrt[n]{z}} = \kappa \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1),$$

where κ is a constant which ought to be the same for all points between A and B on all the curves.

From B onwards it seems that all the additional compound AuCd that is formed is precipitated. Hence, if z_B is the amount in existence at the point B, the active mass of the compound remains constant, and equal to z_B from this point onwards.

The equation of equilibrium then becomes

$$\frac{xy}{\sqrt[n]{z_B}} = \kappa \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2),$$

or, more simply, $xy = \text{const.}$

The flat DE probably corresponds to a state in which the concentration of the cadmium in the liquid is so great that it begins to react with the precipitate, and to form a substance richer in cadmium. Under these circumstances we should expect the cadmium now added to be wholly appropriated, and not to remain in solution. Thus the fall in the freezing point would remain the same until all the insoluble body was transformed. We know that *pure* cadmium in *pure* tin does not give a constant freezing point until 47 atoms of cadmium are present for every 100 atoms of tin, so that the flat DE is caused in some way by the presence of the gold. Analysis of the precipitate beyond E shows it to be richer in cadmium than the formula AuCd requires. See Table XI, Sect. VIII (p. 952).

The second flat, QR, in the curves of Type III also receives a general explanation, for, the equation of equilibrium being still $xy = \kappa z^{\frac{1}{n}}$, we have here x and z constant, for the liquid is saturated with gold and with the compound. It follows that y must also remain constant, even though cadmium be added, that is to say, all the cadmium added is here appropriated by the excess of gold to form more precipitate. Thus the composition of the liquid part remains the same, and therefore the freezing point is constant.

We have not examined the part near R minutely enough to be certain that there is an angle at R like that at B, but it is certain that there is a very abrupt change of curvature here. After R, the explanation of Type III does not differ from that given for Type II, as from that point the liquid is no longer saturated with gold.

The slope from P to Q in the Type III curves corresponds to the part AB in the Type II curves, and is in a general sense intelligible, but the drop from P to Q is not nearly so great as the calculations from the rest of the curves seem to require: in fact, we have here a point where our hypotheses are seen to be imperfect.

Exactly similar phenomena repeat themselves in the curves of Type II, when cadmium is the first metal added to the tin, and gold the second. But in this case the final flat DE occurs at the temperature of the flat QR, and corresponds to the same state.

In order to subject the above considerations to a numerical test, we have carefully re-examined the behaviour of pure gold and pure cadmium, when each of these metals is dissolved by itself in pure tin.

We find that when gold is dissolved in tin its atomic fall is quite constant, and equal to 2·88° up to the concentration of 6·16 atoms of gold per 100 atoms of tin. This is the composition of the eutectic alloy, and further addition of gold causes no further fall.[*] We have carried the addition of gold as far as 11 atoms without producing any change in the freezing point of the eutectic alloy. Thus *a* atoms of gold dissolved in 100 atoms of tin causes a fall of $2{\cdot}88a$, so long as *a* is less than 6·16. In the case of cadmium, the atomic fall is less, even in very dilute solutions, and it decreases somewhat rapidly as the solution becomes stronger in cadmium.

If we denote by $f(y)$ the total fall in the freezing point of the tin caused by dissolving y atoms of cadmium in 100 atoms of tin, then up to $y = 4$ the experiments are well represented by the equation

$$f(y) = 2{\cdot}51y - 0{\cdot}06y^2 \ldots\ldots\ldots\ldots\ldots \quad (3).$$

At the point $y = 4$ there appears to be a slight change, as can be seen by plotting the falls, and the experimental numbers agree better with the equation

$$f(y) = 9{\cdot}08 + 1{\cdot}668(y - 4) - 0{\cdot}01063(y - 4)^2 \ldots\ldots \quad (4).$$

The following Table XII of experimental numbers will serve to verify these equations:—

The following falls produced by gold in tin show that the effect of gold in lowering the freezing point in tin is strictly proportional to the amount of gold added.

---

[*] We believe that not more than 6·16 atoms of gold can dissolve in 100 atoms of tin at the temperature of solidification, in other words, the eutectic alloy is a saturated solution of gold in tin.

TABLE XII.

Atoms of Au per 100 atoms of Sn.	Total fall in degrees centigrade caused by the Au.	Atomic falls.
0·249	0·755	3·02
0·4164	1·20	2·88
0·57	1·63	2·85
1·491	4·27	2·86
2·809	8·01	2·85
3·561	10·31	2·89
3·976	11·47	2·88
5·00	14·43	2·88
5·17	15·04	2·91

TABLE XIII.—*Table of the Fall in Freezing Point caused by adding Pure Cadmium to Pure Tin.*

Atoms of Cd per 100 atoms of Sn.	Total fall in degrees centigrade caused by the Cd.	Atomic falls.
0·0607	0·152	2·5
0·153	0·382	2·5
0·946	2·31	2·44
0·998	2·42	2·44
1·811	4·29	2·37
2·017	4·80	2·38
2·878	6·76	2·348
4·000	9·10	2·28
4·000	9·06	2·265
4·021	9·05	2·25
4·767	10·32	2·165
5·165	10·98	2·116
5·693	11·85	2·085
6·143	12·57	2·046
6·397	12·97	2·028
8·193	15·89	1·94
9·423	17·85	1·894
10·152	18·91	1·862
13·100	23·44	1·789

The change of character in $f(y)$ after $y = 4$ is not due to a change of thermometers or to different samples of cadmium being used.

In the calculations which follow, we have, where it was possible, extracted $f(y)$ from a large-scale curve in preference to using equations (3) and (4).

We can now test the truth of the equations of equilibrium (1) and

(2). *First assume* $n = 1$, *or that the molecule of the compound in solution is* AuCd.

Consider the part between A and B. If we suppose that the free gold and free cadmium each exert the same effect as if the other metal were not there, and that the compound causes the normal molecular fall M, then D being the total fall observed and $F(x)$ the fall caused by x atoms of free gold, we must have

$$F(x) + f(y) + Mz = D \text{ .... } (5).$$

Using the fact that $x = a - z$, $y = c - z$, we may write the above as

$$F(a - z) + f(c - z) + Mz = D.$$

Now $F(a-z)$ is very nearly $2{\cdot}88(a - z)$, but as $F(a)$ can often be obtained by direct observation in the experiment itself, we will replace $F(a - z)$ by $F(a) - 2{\cdot}88z$.

If we also expand $f(c - z)$, we get the following quadratic for z:—

$$\tfrac{1}{2}f''(c)z^2 - [f'(c) + 2{\cdot}88 - M]z = D - F(a) - f(c) \text{ .... } (6).$$

In this equation, $f'(c)$ and $f''(c)$ are the first and second differential coefficients of $f(c)$ and can be got at once from equation (3) or (4).

We must also assume some value for M. In a previous paper, the value of M deduced by the theory of osmotic pressure from Person's value of the latent heat of tin and other constants came out 3°. But our numerous experiments on tin as a solvent lead to the conclusion that this number is a little too great; we have therefore in what follows taken $M = 2{\cdot}88$.

Equation (6) is thus by means of equation (3) reduced to the form

$$z^2 + (41{\cdot}83 - 2c)z = \frac{f(c) + F(a) - D}{0{\cdot}06} \text{ ...... } (7).$$

If c were much greater than 4, we ought to use the other form derived from equation (4), namely:

$$z^2 + (164{\cdot}92 - 2c)z = \frac{f(c) + F(a) - D}{0{\cdot}01063} \text{ ...... } (8).$$

In these equations, the three quantities in the numerator of the fraction on the right are experimental numbers. In a series of experiments in which gold was the first metal added, $F(a)$ is the total fall caused by the gold, $f(c)$ is taken from a curve plotted from the table of cadmium falls, and D is the total observed fall caused by the mixture of cadmium and gold. There is but little error if we neglect z^2 in these equations, and Table XIV (p. 961) can be quickly verified by thus treating (7) as a simple equation.

The following table, XIV (next page), gives the values of z, x, and $\kappa = xy/z$ for points between A and B on the different curves. It was drawn up by solving equation (7) as a quadratic.

It is evident from this table that for very different concentrations, from 0·5 to 5 atoms of gold and 0 5 to 4 atoms of cadmium, the value of κ does not vary much from the mean value of 8 8, while z increases to a somewhat uncertain maximum at the point B.

It must be remembered in judging of the constancy of κ that the value of z is very nearly proportional to the experimental number $F(a) + f(c) - D$, and that this, which depends on three experiments made at different times, is a small difference of temperature ranging from 0 3° to 1 6°. Thus small errors of observation cause a large percentage error in z and a larger one in κ, which is $\frac{(a-z)(c-z)}{z}$.

In fact the constant κ is very sensitive to experimental errors and such errors would account for larger fluctuations of κ than are seen in the table.

There are, however, other causes of variation at work, for with much gold κ has high values and with much cadmium low values. At the point $a = 1, c = 7$ of a series of experiments in which 7 atoms of cadmium were added and then gold, the value of κ calculated as in the table is $\kappa = 4·3$, and other points in this 7-atom cadmium curve give values of κ which are much too low. Here the large amount of cadmium has altered the conditions so that the free gold in the liquid does not produce quite its usual fall.

The theory of osmotic pressure, in fact, warns us that this must occur, for the presence of the cadmium lowers the osmotic pressure exerted by the gold in two ways, by lowering the freezing temperature, and, also, probably by increasing the volume of the alloy.

The gold, for an unknown reason, perhaps because it appropriates tin and so decreases the amount of the solvent, has an opposite effect. It maintains its own effect undiminished right up to saturation and it probably increases the effect of any other metal which is in the same solution but not combined with it.

It might be possible to apply corrections for these disturbing causes, but for the present we propose to consider only those moderately dilute solutions where they do not have much effect.

The Part BCD *of the Curves.*—After the angle B we must suppose that the tin has become saturated with the compound, the amount z_B, which was formed at B, alone remaining in solution, however much may be formed.

The resulting equation of equilibrium $xy/z_B = \kappa$, or $xy =$ const., explains a very marked feature in the curves, namely, that a maximum freezing point, that is, a *minimum fall*, occurs when the number

TABLE XIV.—*Table for the part AB of the Curves giving z, x, y, and $\kappa = \frac{xy}{z}$, calculated from the Equation*

$$z^2 + (41{\cdot}83 - 2c)z = \frac{F(a) + f(c) - D}{0{\cdot}06}.$$

Table.	a.	c.	D.	F(a).	$f(c)$.	z.	x.	y.	κ.	—	κ. Au_4Cd_3
I and II	2·0	0·5	6·7	5·68	1·25	0·093	1·907	0·407	8·3		4·93
"	2·0	1·0	7·73	"	2·43	0·16	1·84	0·84	9·9		7·7
"	2·0	2·0	9·76	"	4·77	0·30	1·7	1·7	9·6		10·8
"	2·0	3·0	11·77	"	7·01	0·42	1·58	2·58	9·7		13·47
"	2·0	4·0	13·55	"	9·08	0·58	1·42	3·42	8·3		13·60
III	3·01	0·5	9·60	8·67	1·25	0·131	2·88	0·369	8·1		6·06
"	3·01	0·99	10·51	"	2·41	0·237	2·77	0·753	8·8		8·86
"	3·01	1·99	12·84	"	4·75	0·452	2·56	1·538	8·7		—
"	3·01	2·99	14·18	"	6·99	0·662	2·35	2·37	8·3		15·4
IV	4·0	0·5	12·27	11·36	1·25	0·138	3·86	0·362	10·1		6·27
"	4·0	1·0	13·14	"	2·43	0·27	3·73	0·73	10·1		10·9
"	4·0	1·5	13·98	"	3·60	0·416	3·58	1·081	9 3		—
"	4·0	1·85	14·58	"	4·42	0·538	3·46	1·312	8·4	Angle B	13·7
V	5·0	0·5	15·27	14·43	1·25	0·167	4·83	0·833	9·7		8·57
"	5·0	1·0	16·06	"	2·48	0·331	4·67	0·669	9·4		11·8
"	5·0	1·59	16·91	"	3·81	0·564	4·44	1·03	8·1	Angle B	13·7
IX	0·5	4·0	10·17	—	9·06	0·161	0·339	3·84	8·1		7·3
"	1·0	4·0	11·28	—	"	0·321	0·679	3·679	7·8		10·0
"	2·0	4·0	13·5	—	"	0·637	1·363	3·363	7·2		13·5
"	2·49	4·0	14·63	—	"	0·765	1·725	3·235	7 3	Angle B	15·0

of atoms of gold and of cadmium in the block is equal. It does not matter whether we start a series with 4, 5, 6·6, or 9 atoms of gold, or with 4 atoms of cadmium, we always reach the summit C at a constant temperature when the number of atoms of the second metal added equals that of the first. The explanation on the hypothesis of the formation of the body Au_nCd_n is obvious. A minimum fall means a minimum number of molecules in solution. So that at C, $x + y$ must be minimum with the condition $xy = \text{const.}$

It is well known that under this condition the minimum is reached when $x = y$, and as $a - x = c - x$ it follows that $c = a$.]

This agreement of experiment with the theory seems a strong confirmation of the latter.

We can apply a numerical test to the equation $ay/z_B = \kappa$, as before. The equation to obtain z is now

$$F(a - z) + f(c - z) + 2{\cdot}88z_B = D \;\ldots\ldots\ldots \quad (9).$$

This can be reduced to a quadratic, as before.

If $c - z$ is less than 4, we use equation (3), and so obtain

$$z^2 + (89{\cdot}83 - 2c)z = \frac{F(a) + f(c) + 2{\cdot}88z_B - D}{0{\cdot}06} \;.. \quad (10).$$

z_B is somewhat uncertain, but from Table XIV it seems to be not far from the value 0·6. We shall use this value.

Where the gold is added first, and the tin is not saturated, we have used the value of $F(a)$, obtained from the particular experiment under discussion, but when gold is the second metal, or, as in the 6·6- or 9-atom gold curves, we have been obliged to use $F(a) = 2{\cdot}88a$. If c was less than 4, $f(c)$ was taken from a large-scale curve, but in the case where c was greater than 4, whilst $c - z$ was less than 4, $f(c)$ was taken from equation (3). In the numerous cases where $c - z$ turned out to be greater than 4, we used equation (4) to reduce equation (9), thus getting, instead of (10), the equation

$$z^2 + (435{\cdot}84 - 2c)z = \frac{F(a) + f(c) + 2{\cdot}88z_B - D}{0{\cdot}01063} \;\ldots. \quad (11).$$

In the following table, XV, the first column indicates which of equations (10) or (11) has been used.

The table shows that, with one or two exceptions, where the concentrations are extreme, κ does not differ much from a mean value of 9.

The value of x and y at the summit C is very constant: $x = y = 2{\cdot}31$.

TABLE XV.—*Table for the part* BCD *of the Curves giving* z, x, y, *and* $\kappa = \frac{xy}{0 \cdot 6}$, *calculated by means of Equations* (10) *and* (11).

Table	a.	c.	D.	F(a).	$f(c.)$	z.	x.	y.	κ.	
I and II	2·0	5·0	15·05	5·68	10·74	0·68	1·32	4·32	9·3	(11).
" "	2·0	7·0	16·97	"	13·99	0·985	1·01	6·01	10·2	(11).
III	3·0	4·0	14·24	8·67	9·08	1·05	1·95	2·95	9·6	(10).
"	3·0	6·0	15·07	"	12·35	1·69	1·81	4·31	9·4	(11).
IV	4·0	3·0	14·10	11·47	7·01	1·20	2·80	1·80	8·4	(10).
"	4·0	4·0	13·88	"	9·08	1·68	2·32	2·32	9·0	(10) Summit C.
"	4·0	7·0	15·47	"	18·99	2·60	1·4	4·4	10·3	(11).
"	4·0	10·0	18·49	"	18·68	3·01	0·99	6·90	11·5	(11).
"	4·0	11·75	20·58	"	—	3·24	0·76	8·51	10·8	(11) Angle D.
V	5·0	3·0	14·71	14·43	7·01	1·65	3·35	1·35	7·5	(10).
"	5·0	5·0	18·84	"	11·01	2·69	2·31	2·31	8·9	(10) Summit C.
VI	6·6	2·48	18·62	19·01	5·76	1·52	5·08	0·91	7·7	(10).
"	6·6	6·6	18·77	"	13·95	4·30	2·3	2·3	8·81	(10) Summit C.
"	6·6	10·0	15·62	"	18·67	5·32	1·28	4·68	10 0	(11).
"	6·6	14·53	20·81	"	25·65	5·83	0·77	8·7	11·2	(11) Angle D.
VII	9·0	6·0	15·46	25·92	12·9	5·05	3·95	0·95	6·3	(10).
"	9·0	9·0	13·81	"	17·73	6·7	2·30	2·30	8·82	(10) Summit C.
"	9·0	13·0	16·56	"	28·20	7·74	1·26	5·26	8·9	(11).
"	9·0	16·45	20·61	"	30·96	8·68	0·32	7·77	4 1	(11)* Angle D.
IX	3·0	4·0	14·17	8·64	9·06	1·06	1·94	2·94	9·5	(10).
"	4·0	4·0	13·82	11·52	"	1·69	2·31	2·31	8·9	(10).
"	6 0	4·0	14·61	17·28	"	2·65	3·35	1·35	7·5	(10).
"	8·88	4·0	18·74	25·57	"	3·44	5·44	0·56	5·1	(10).*

---

* In these cases where the greater part of one of the metals has been removed from the solution, a small percentage error in z causes a large error in κ.

Hence we see why the 2-atom gold curve cannot have a summit, for $x = 2\cdot3$ implies $a = 2\ 9$. The 3-atom gold curve is just on the border-line between Type I and Type II.

κ *Deduced from Analyses.*

Table XI (pp. 951, 952) contains the analyses of the liquid alloy at four points on the part BCD of the curves; and these analyses can be used to calculate x, y, z, and κ, instead of employing the freezing point determinations. In Table XVI, Columns 1 and 2 contain the original composition of the mixture in the block, expressed as usual in terms of a and c. Column 3 contains the mean of two or more analyses, in each case, of the liquid alloy. Column 4 contains the number of atomic weights of gold and cadmium per 100 atomic weights of tin, calculated from Column 3. Column 5 contains the values of x and y, obtained by subtracting 0·6 from each of the numbers in Column 4. In column 6 is given κ or $xy/0\cdot6$. As by the theory $z = a - x = c - y$, we have tabulated under z the values of these two quantities as deduced from the analyses: they ought of course to be equal.

TABLE XVI.—*Table of κ deduced from Analysis.*

1	2	3			4	
a.	c.	Sn.	Au.	Cd.	Au.	Cd.
4·0	7·0	91·76	3·52	4·72	2·3	5·42
5·0	5·05	92·52	5·03	2·45	3·25	2·79
13·98	9·22	89·8	8·7	1·49	5·8	1·75
11 0	8·78	92·2	5·78	2·08	3·75	2·38

5		6	z.	
x.	y.	κ.	$a - x$.	$c - y$.
1·7	4·82	13·6	2·3	2·18
2·65	2·19	9·7	2·35	2·86
5·2	1·15	10·0	8·8	8 0
3·15	1·78	9·4	7·85	7·0

It can be seen from the table that the results of the analyses are quite consistent with the equation of equilibrium, although they afford results inferior in accuracy to the freezing point determinations.

The preceding results appear to us to prove that the gold and cadmium combine in the ratio Au : Cd; but the proof that the molecule of the compound, when in solution, is AuCd, and not Au_2Cd_2, or Au_3Cd_3, &c., is much weaker. The results of the analyses, and the common temperature at the summit C, of course, throw no light on this point.

We might hope to solve it if the body were more soluble, by calculating tables of κ for other values of n, and the examination of the part AB, by means of the formula Au_2Cd_2, does throw the only light we have on the matter. If we assume Au_2Cd_2, the equation of equilibrium for the part AB is $xy/\sqrt{z} = \kappa$, a constant, and the equation to get z is

$$z^3 + (32{\cdot}917 - c)z = \frac{F(a) + f(r) - D}{0{\cdot}24}.$$

The resulting values of κ are tabulated in the extreme right-hand column of Table XIV (p. 961). It will be seen that the numbers in the column are not at all constant, but vary from 5 to 15. If we keep the gold constant, κ increases *pari passu* with the amount of cadmium added.

Thus the formula Au_2Cd_2 does not, for the part AB, agree with the experimental facts. The formula Au_3Cd_3 also fails to give a constant κ.

When we consider the part BCD, we find κ equally constant, whether we use the formula AuCd or Au_2Cd_2; and this clearly should be the case, for in this part of the curves the bulk of the compound is out of solution, and so its molecular weight becomes of less importance. The equation of equilibrium, $xy =$ constant, is of the same form, whatever value of n we take.

Thus, the only part of the curve that can help us to decide the molecular weight of the compound is the part AB, and the values of κ deduced from this, point pretty clearly to the molecular formula AuCd.

Description of the Plates.

The plates (see next page) represent the fall below the freezing point of pure tin of an alloy of gold and cadmium.

The number of atomic weights of foreign metals present per 100 atomic weights of tin is indicated by the numbers counted from left to right. The observed fall in the freezing point in degrees centigrade is indicated by the numbers counted vertically downwards from 0.

Down to the point A, only one metal (gold in every case but one) was added to the tin. The part beyond A corresponds to the addition of the second metal.

In Plate 1 we have curves of Type I, which may be called the 2- and the 3-atom gold curves. In Plate 2 we have Type II, the 4- and 5-atom gold curves, and the 4-atom cadmium curve. This latter is shifted five spaces to the right, to avoid confusion. Plate 3 contains the saturated gold curves, in which 6·6, 9, and 11 atoms of gold, respectively, were first added. In the upper part of Plate 3 is seen the part PQ of the 11-atom gold curve which is due to the first additions of cadmium. This portion was examined with especial care.

The curves here given are merely intended to serve as diagrams, but in order to calculate the tables of z and κ the original numbers have been charted on the scale of two degrees or two atoms to a decimetre. Even on this large scale most of the experimental points lie *on* the curve.

A 7-atom cadmium curve has been worked through, and has the same character as the 4-atom curve, but it is not given in the plates.

In conclusion, we must express our best thanks to Miss Field, of Newnham College, for her able assistance in making a large number of freezing point determinations and analyses.

We are also much indebted to Dr. G. H. Milnes for making several control analyses.

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Cambridge.

LXXXIII.—*The Sulphonic Derivatives of Camphor.*

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The substitution derivatives of camphor do not at present lend them- to systematic classification or to prediction of the number of possible isomers. The preparation of any new derivative of camphor will, therefore, possess an interest of its own, apart from any question of the constitution of the compound. It will in all probability be necessary to prepare a large number of such compounds before we find our-

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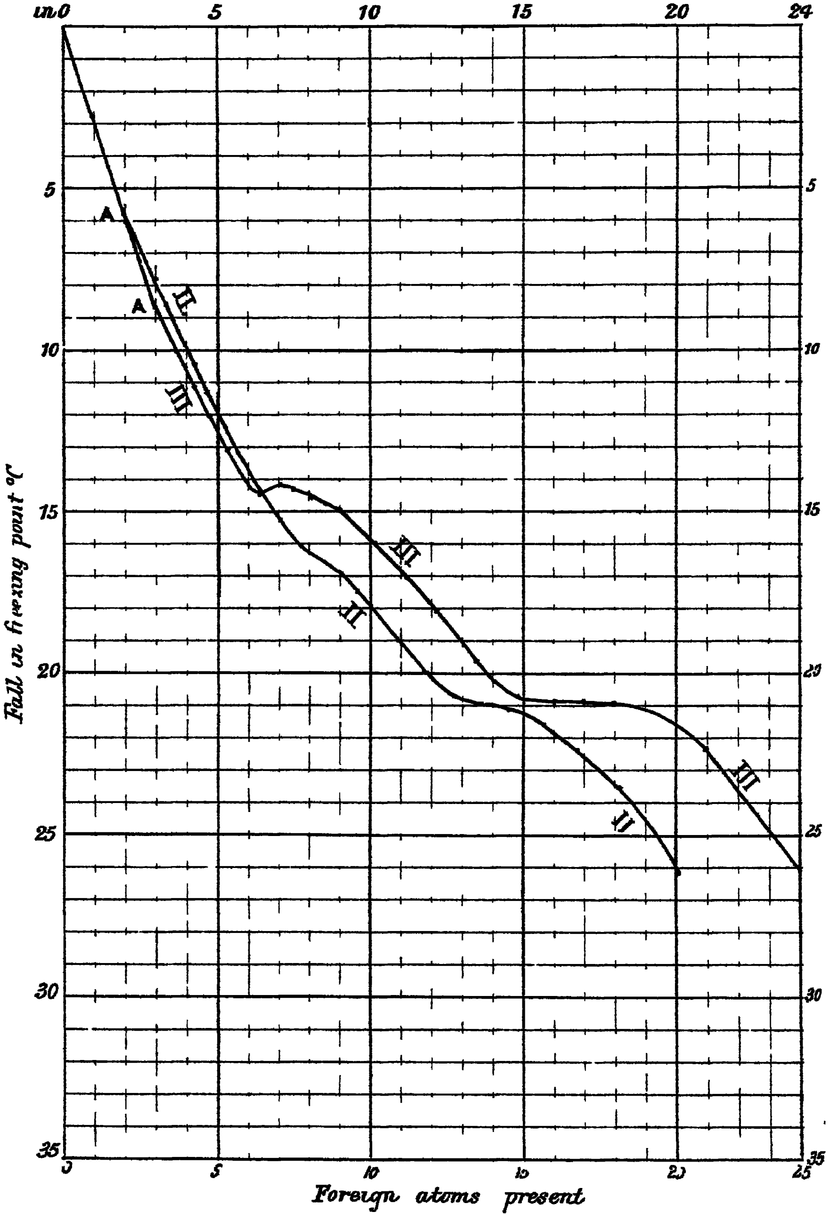
PLATE I.



Roman numerals refer to the tables

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PLATE 2.

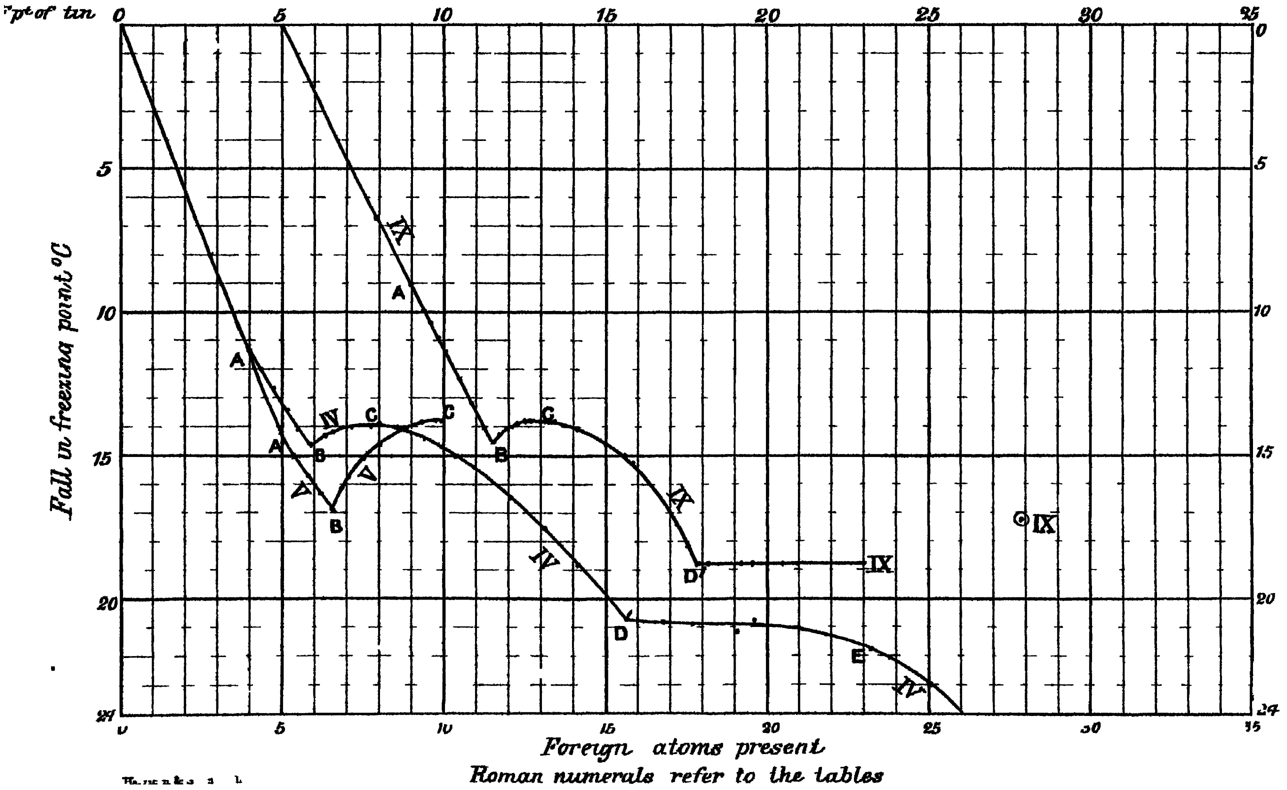
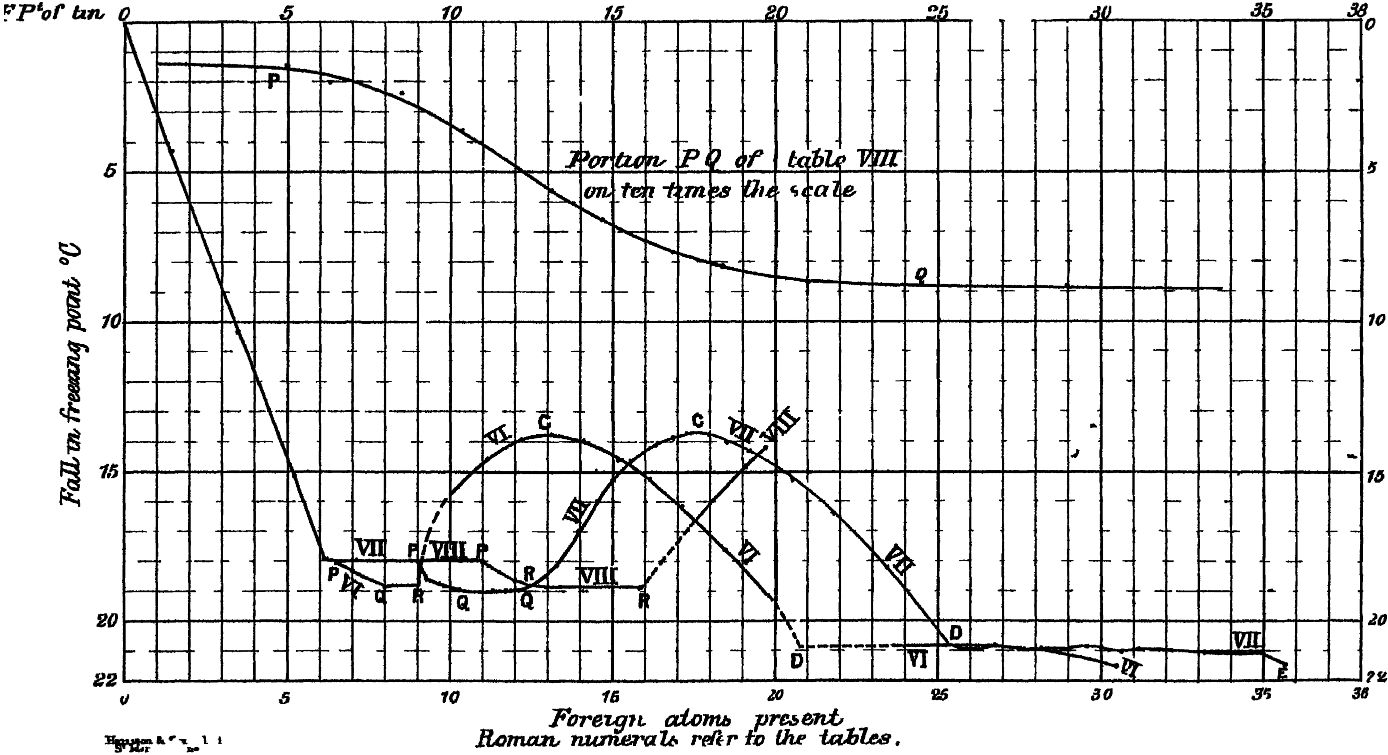


PLATE 3


F.P.t of tin
Fall in freezing point °C
Foreign atoms present
Roman numerals refer to the tables.
Portion PQ of table VIII
on ten times the scale
0
5
10
15
20
25
30
35
38
22
P
Q
VI
VII
VIII
C
D
E
R
F

selves in a position to speculate with any confidence as to their atomic arrangements.

We have been acquainted for some time with chloro-, bromo-, and nitro-derivatives of camphor, but not with any compounds in which hydrogen is replaced by the sulphonic group SO_3H. The action of sulphuric acid on camphor did not yield either to Chautard (*Compt. rend.*, **44**, 66), to Schwanert (*Annalen*, **123**, 298), or to Kachler (*ibid.*, **164**, 90) any sulphonic acid, nor did Cazeneuve (*Compt. rend.*, **110**, 719) by the same reaction, or by that of sulphuric acid on the bromo- and chloro-camphors, observe any simple displacement of hydrogen by the sulphonic group, but rather compounds were formed which indicated a considerable and peculiar decomposition of the camphor nucleus.

Camphor we know does not yield directly a nitro-camphor, whereas bromo- and chloro-camphor, when treated with nitric acid, do give nitro-derivatives. Thus it seemed not improbable that, though camphor itself might be incapable of giving directly a sulphonic derivative, we should yet be able to obtain the corresponding compounds from the haloid camphors. This we have in fact been able to do by employing chlorosulphonic acid, $ClSO_3H$, dissolved in chloroform for the sulphonation, instead of sulphuric acid. Camphor itself yields no sulphonic acid by this treatment. We have continued the work begun by one of us (Trans., 1890, **57**, 828), and have prepared a number of derivatives of the sulphonic acids of the isomeric bromo- and chloro-camphors. These compounds we describe in the subsequent pages. At the same time, there are some remarks of a general character which we wish to make before entering into experimental detail.

In the first place, as to rotatory power, the sulphonic compounds have been found to rotate the plane of polarised light, a property hitherto observed in very few sulphur compounds, and not at all in any sulphonic acid. This optical activity affords an instance of the remarkably stable nature of the asymmetric carbon atom or atoms in the camphor nucleus, in striking contrast to their comparative instability in the case of other active substances. As another instance of this which has come under our observation, we have found that camphoric acid retains its optical activity unimpaired by the distillation of its anhydride through a red-hot tube, whereby a considerable part of it is decomposed; the recovered camphoric acid has, if anything, a higher rotation after this treatment than it possessed before.

Another point of interest is that the isomerism established between the respective chloro- and bromo-camphors, obtained by direct action of the halogen, is maintained in their sulphonic derivatives, and is characterised especially by the difference in rotatory power. This difference corresponds with that between the bromo-camphors themselves; for example, the sulphonic compounds of the α-bromocamphor of sp. rot. +135° show a greater activity than those of the β-bromocamphor of sp. rot. +30°.

Many of the sulphonic compounds are uncrystallisable, and, being also non-volatile, are difficult to purify. Some of the salts, however, crystallise well, and they have been studied in particular from two points of view, both as to their capability or not of crystallising, and as to their rotatory power. In neither case, however, could any general conclusion be drawn. It appeared at one time that the salts of metals of low atomic weight crystallised, whilst those of metals of high atomic weight did not, but from the impossibility of obtaining a crystalline lithium salt this view had to be abandoned. The rotatory power of these salts, as well as the salts of active acids generally, involves us in the vexed question of the nature of solution. If salts in dilute solution are completely dissociated into their ions, then the salts of an active acid should all have the same rotatory power, which would also be that of the acid itself, since the optically active ion would in every case be the same. Experiments are being continued in this laboratory to investigate this point further. So far, our own experiments, as well as those of Landolt on the tartrates, do not appear to support the dissociation theory. Landolt, in fact, obtained specific rotation values for the tartrates, of very various concentrations, it is true, lying between 20·64°, the value for sodium arsenyl tartrate, and 142·76°, the value for tartar emetic.

As to the chemical properties of the camphorsulphonic acids, fusion with potash of the α-bromo-acid splits off the sulphonic group which appears as sulphite, but nothing could be made of the compound or compounds formed; a profound decomposition appeared to have taken place. Nitric acid brings about a displacement of the sulphonic group, with production, in the case of the α-bromo-acid, of the ordinary nitrobromocamphor. In the case of the β-bromo-acid, a new isomeric nitrobromocamphor appeared to be formed, but it was not obtained sufficiently pure to merit a detailed description. Bromine-water produces a slight precipitation in a solution of the α-bromosulphonic acid in the cold, but we are unable at present to show whether or not the sulphonic group is replaceable by bromine.

Preparation of the Bromocamphors.

Camphor was brominated in alcoholic solution by the method already described (Trans., 1890, 57, 828), and the two isomeric bromocamphors separated by fractional crystallisation from light petroleum. In the later experiments, the volatile products of the bromination were led, by means of a bent tube, into a vessel containing water. A volatile oil was thus collected as a heavy layer beneath the hydrobromic acid, and was found to be pure ethyl bromide. Ethyl bromide may be obtained in considerable quantity in this way as a byeproduct.

By recrystallising the crude β-bromocamphor four times (an operation extending over many weeks) a product was obtained which gave for 2·1243 grams in 25 c.c. a value corresponding to

$$[\alpha]_D = +29\cdot4^\circ.$$

The value previously found for the rotation of the β-isomer was +34·9°.

This lower value is, therefore, more nearly the true rotation value for the new isomer, as any impurity, such as unaltered camphor or α-bromocamphor, would tend to increase the value observed.

The yield of pure α-bromocamphor obtained was about 50 per cent. of the theoretical; besides this, 20 per cent. of isobromocamphor was obtained and 20 per cent. of a mixture of the two isomerides.

A small amount of an oil, which solidifies in a freezing mixture, was also obtained, but the attempts to purify it were not successful. The probability is that it is a liquid dibromocamphor containing β-monobromocamphor. This oil reacts very violently with strong nitric acid in the cold, and, on distilling the product in steam, a yellow, semi-solid substance passes over, which, on analysis, proved to be dinitrodibromocamphor, a compound hitherto unknown.

Bromine Determination by Carius' Method.

I. 0·2360 gram substance gave 0·2142 AgBr and 0·0023 Ag.

II. 0·2400 gram of another specimen gave 0·2163 AgBr.

		Found.	
	Theory.	I.	II.
Br......	40·00 per cent.	39·34	40·8 per cent.

N Determination.

0·9460 gram substance gave 54·5 c.c. of moist N at 13° and 767 mm. b. p.

	Theory for $C_{10}H_{12}Br_2O(NO_2)_2$.	Found.
N........	7·00 per cent.	6·77 per cent.

The two specimens of bromocamphor used in subsequent experiments had the following melting points and rotatory power:—

	M. p.	$[\alpha]_D$.
α-Bromocamphor	76°	+132·0°
β-Bromocamphor	61	+ 29·4

The α-compound was colourless and crystalline, and of a hard and brittle texture, whilst the β-compound was soft, yellowish, and of a camphorous consistency.

Sulphonation of α-Bromocamphor.

In the following experiments it was found that on treating 1 mol. of bromocamphor with 1 mol. of chlorosulphonic acid, only about 40 per cent. of the camphor was sulphonated:—

$$C_{10}H_{15}BrO + ClSO_3H = HCl + C_{10}H_{14}BrO{\cdot}SO_3H.$$

This equation, however, merely expresses the preliminary reaction, for the free sulphonic acid reacts with the excess of chlorosulphonic acid to produce the acid chloride and sulphuric acid, thus:—

$$C_{10}H_{14}BrO{\cdot}SO_3H + ClSO_3H = C_{10}H_{14}BrO{\cdot}SO_2Cl + H_2SO_4.$$

By employing two equivalents of chlorosulphonic acid, the yield was more than doubled, and in one experiment as much as 95 per cent. of the theoretical amount of the barium salt of the α-bromosulphonic acid was obtained.

In the first experiments, a weighed quantity of bromocamphor, which had been dried for several days over sulphuric acid, was dissolved in the least amount of chloroform, previously freed from alcohol, and the chlorosulphonic acid added. The product always appeared rather charred and difficult to decolorise, but by using a much larger quantity of chloroform, preferably twice the weight of the bromocamphor taken, a much cleaner product was obtained, though the gross yield of sulphonate weighed as barium salt was not quite so great as when the more concentrated solutions were employed. The following is the description of a recent experiment:—

82 grams of pure, dry α-bromocamphor were placed in a round flask of 500 c.c. capacity, and 164 grams of chloroform, specially purified and dried, were added, when the bromocamphor was quickly dissolved. To ensure complete absence of moisture, the solution was shaken up with finely powdered calcium chloride, left for 24 hours, filtered, and the clear liquid put into a round flask fitted with a reflux condenser. The whole apparatus was placed on a water-bath in the draught chamber, although no heat was applied until it was required to hasten the reaction, and 82 grams of recently prepared chlorosulphonic acid was introduced by a tap funnel down the condenser. The liquid in the flask became perceptibly warm, although the action was not by any means violent.

A calcium chloride drying tube was now fitted to the top of the condenser, and the flask gently heated on a water-bath, when a lively reaction set in, and torrents of hydrogen chloride were evolved. This evolution of hydrogen chloride ceased after 9 hours heating, but to ensure the completion of the reaction the heating was continued for 12 hours longer, at the end of which time the liquid had separated into two layers.

The whole mass was then poured into cold water, whereby an upper stratum of brownish-yellow solution and a heavy black oil were obtained. The latter was drawn off and dried with calcium chloride, and the chloroform evaporated, when the residue was found to be nearly all α-bromocamphorsulphonic chloride, together with an insignificant amount of unaltered bromocamphor.

The upper, aqueous solution took 115 grams of barium carbonate for complete neutralisation, and after filtering from the barium sulphate gave a brownish-yellow solution, which was evaporated to the consistency of a dense syrup on the water-bath; on treating this with methylated spirit, a small residue of barium carbonate and chloride was left undissolved, and the filtrate, on concentration, left a brown and dense syrup which we were unable to obtain crystalline. It was, therefore, dried at 115° in an air-bath, and after rapidly pulverising in a mortar, was quickly transferred to a stoppered bottle and employed as raw material for the preparation of the other derivatives of the α-bromocamphorsulphonic acid.

The extremely deliquescent nature of the salt renders it rather troublesome to deal with, but it is stable as compared with the potassium and lithium salts, which deliquesce so eagerly (when anhydrous) that when left in the open air they become liquid or pasty in less than a minute. The highly deliquescent nature of the lithium salt rendered it necessary to dehydrate it in a tube drawn out to a capillary point, which was sealed as soon as the salt was dry.

α-Bromocamphorsulphonic Acid and its Salts.

α-Bromocamphorsulphonic Acid, $C_{10}H_{14}BrO\cdot SO_3H$.—To prepare the acid, 10 grams of the barium salt (see below) were dissolved in water, and dilute sulphuric acid run in until all the barium was precipitated. The filtrate was evaporated on the water-bath, extracted with absolute alcohol, and the alcoholic solution again evaporated. In this way a black, tarry mass was obtained which solidified on standing over sulphuric acid in a vacuum. It was soluble with great ease in water, producing a strongly acid liquid which evolved hydrogen when heated with zinc or magnesium.

Barium Salt, $(C_{10}H_{14}Br^{\alpha}\cdot SO_3)_2Ba$.—This barium salt is soluble in water, and also in alcohol, but much more readily in the former. It is practically insoluble in ether, benzene, chloroform, and carbon bisulphide.

The analysis gave the following results:—

I. 0·4078 gram substance gave 0·1258 gram $BaSO_4$.
II. 0·4858 ” ” 0·1514 ”
III. 0·2880 gram was oxidised to 0·1718 ”

	Found.			Theory.
	I.	II.	III.	
Ba	18·13	18·32	—	18·09
S	—	—	8·19	8·45

The aqueous solution of the salt was so dense that trustworthy values for the rotatory power were not obtainable. It was, however distinctly dextrorotatory.

The *potassium salt*, $C_{10}H_{14}BrO\cdot SO_3K$, is highly deliquescent, and readily becomes liquid in the open air.

A hot, alcoholic solution of the anhydrous salt on one occasion deposited a small crop of microscopic crystals on cooling; a few minutes exposure to the air, however, caused them to deliquesce, and to dissolve again in the mother liquor, showing the intense affinity of the anhydrous salt for water. The potassium salt was used for making the sulphonic chloride, and will be referred to again under that head.

The *Sodium Salt*, $C_{10}H_{14}BrO\cdot SO_3Na$.—This was prepared from the barium salt by dissolving 10 grams of it in hot water, and adding a solution of sodium carbonate as long as a precipitate of barium carbonate appeared. The solution was then concentrated by evaporation, and, on cooling, solidified to a crystalline mass. This was recrystallised from a very little boiling water, filtered, and dried on a porous tile. It was of a silky texture, and almost colourless. It melted to a colourless liquid at 52°.

Rotation of Sodium Salt in Aqueous Solution.

1·0762 grams in 25 c.c. at 15° gave for 20-decimetre tube $\alpha = +6·0°$;

$$\therefore [\alpha]_D = +76·4°.*$$

Analyses of Sodium Salt.

I. 0·3442 gram substance lost 0·0602 gram water at 100°.
0·3442 ” ” 0·0729 ” ” 135°.
II. 0·2812 ” ” 0·0589 ” ” 135°.

---

* As the salt contained 5 mols. H_2O, $[\alpha]^D$ is referred to the anhydrous salt.

	Found.		
	I.	II.	Theory.
$4H_2O$............	17·48	—	17·77
$5H_2O$.....	21·17	20 94	21·04

III. 0·3442 gram substance gave 0·0527 gram Na_2SO_4.
IV. 0·2812 „ „ 0·0465 „

	Found.		
	III.	IV.	Theory.
Na..........	4·96*	5·35	5·43

The *ammonium salt*, $C_{10}H_{14}O·SO_3NH_4$, was prepared as follows:—10 grams of the barium salt were dissolved in hot water, and 3 grams of ammonium sulphate added. After filtering off the barium sulphate, the solution was evaporated on the water-bath and extracted with alcohol, which left a small quantity of ammonium sulphate undissolved. On evaporating the alcoholic solution, a semi-crystalline mass was obtained; this was dissolved in a few drops of hot water, and on cooling it became semi-solid. The white, silky needles were collected and recrystallised. On heating to 270°, the substance darkened, and melted with an almost explosive decomposition.

Rotation Determination.

1·1426 grams salt were dissolved in 25 c.c. of water.

$$l = 10\,;\ \alpha = +4^\circ\ 0''\,;\ \therefore\ [\alpha]_D = +87^\circ.$$

Sulphur Determination, Carius' Method.

I. 0·2112 gram substance gave 0·15045 gram $BaSO_4$.
II. 0·3171 „ „ 0·2214 „

	Found.		
	I.	II.	Theory.
Sulphur..........	9·78	9·89	9·75

Magnesium Salt.—This was first prepared by dissolving metallic magnesium in a dilute solution of the free sulphonic acid in water; hydrogen was thus freely given off, especially on warming. To ensure complete saturation of the acid, the solution was boiled with a little magnesia until quite neutral to litmus, and then filtered and evaporated. An almost colourless, crystalline product was thus obtained, which dried up over sulphuric acid to a crisp, dry powder.

---

* Slight loss by spirting.

Rotation Determination.

$$T = 14^\circ,\ \text{Solvent } H_2O,\ l = 10,\ C = 1{\cdot}1896 \text{ in 25 c.c.},\ \alpha = 1^\circ\ 20'';$$
$$\therefore [\alpha]_D = +27^\circ\ 9.$$

The *zinc salt* is more deliquescent and less crystalline than the corresponding magnesium salt.

a-Bromocamphorsulphonic Chloride, $C_{10}H_{14}OBr{\cdot}SO_2Cl$.

To prepare this, 20 grams of the dried potassium salt were mixed with the calculated weight of phosphorus pentachloride in a porcelain mortar, when an energetic reaction took place, and the mixture soon became liquid. After about five minutes, when the action appeared over, the brownish, viscid liquid was poured into a considerable volume of water; oily flakes were then thrown down which rapidly solidified. These were collected, dried as far as possible, and dissolved in chloroform; after drying the chloroform solution with powdered calcium chloride, it was evaporated on the water-bath, when it left a black, viscid oil. This smelt and tasted like an acid chloride, and, on standing over sulphuric acid in a vacuum, solidified to a black semicrystalline solid.

Analysis by Carius' Method.

0·3577 gram substance gave 0·4344 gram of mixed AgCl and AgBr.

	Found.	Calculated.
Cl	10·70	10·77
Br....	24·11	24·27

This sulphonic chloride is remarkably stable towards water, and is not completely converted into acid, even after prolonged boiling with it. Dilute soda solution, however, rapidly decomposes it.

The action of strong aqueous ammonia on the sulphonic chloride produces a mixture of amide and ammonium salt; the latter being soluble in water is easily separable from the amide, which remains as a brown, viscid oil.

The chloride dissolves in alcoholic ammonia with a brown coloration and considerable production of heat. On evaporation, a sticky, brown tar is left, which eventually crystallises if left for two or three months.

Aniline reacts powerfully with the sulphonic chloride with production of an anilide. Like the amide, this is extremely difficult to purify, and has not yet been obtained definitely crystallised.

Sulphonation of β-Bromocamphor.

As sulphonation in a concentrated chloroform solution produced a considerable darkening in colour, and might be expected to effect a more or less extended conversion of the β-derivative into the corresponding α-modification, the operation was finally carried out in a fairly dilute solution. To compare and contrast the two isomers, equal quantities of α- and β-bromocamphor were similarly sulphonated under identical conditions.

In a comparative experiment, 82 grams of the respective bromocamphors, 164 grams of chloroform, and 82 grams of chlorosulphonic acid were employed, the chloroform solution being carefully dehydrated by powdered calcium chloride. A marked difference was noticed in the two reactions. The β-compound from the first reacted with a perceptible development of heat, and free evolution of hydrogen chloride; whilst the product of the sulphonation of the α derivative became black, that of the β-compound remained of a light-reddish tinge. The α-product required 115 grams of barium carbonate for complete neutralisation, whilst the β- took only 105 grams. About the same quantity of pure barium salt was obtained in each case, namely, 76 grams, the chloroform solution containing sulphonic chloride with a trace of the unaltered bromocamphor.

Barium β-Bromocamphorsulphonate, $(C_{10}H_{14}OBr \cdot SO_3)_2Ba$.—The barium salt was obtained as a thick, brown syrup on evaporating its aqueous solution on the water-bath, and required heating to a temperature of 125° to drive off the excess of water; a crisp, powdery solid was thus obtained having a great affinity for moisture. An analysis gave the following result:—

0·3450 gram substance gave 0·1067 gram $BaSO_4$.

	Found.	Theory.
Ba	18·10	18·09

Sodium β-Bromocamphorsulphonate, $C_{10}H_{14}OBr \cdot SO_3Na$.—5 grams of the barium salt were dissolved in water, and a solution of sodium sulphate added as long as a precipitate was formed. The filtrate was evaporated to a thick syrup on the water-bath, extracted with alcohol, filtered. and again evaporated down until fairly concentrated. The α-salt, under similar conditions, crystallised in silky, white needles. The β-salt absolutely refused to crystallise even when placed in a vacuum over sulphuric acid for a week. Under these circumstances, however, it solidified to a transparent, deliquescent mass, which, on heating at 120°, gave off water, and was obtained in the anhydrous condition. It is of interest to note that, whilst the β-salt retains its 2 mols. of water of crystallisation at 100°, the α-salt loses 4 mols. H_2O at this temperature, and retains one only.

Rotation in Aqueous Solution 14°.

0·8555 gram anhydrous salt in 25 c.c.

$$l = 20, \alpha = +0{\cdot}50''; [\alpha]_D = +12{\cdot}2°.$$

$$\alpha\text{-}Salt, [\alpha]_D = +76{\cdot}4.$$

Analyses of the β-Sodium Salt.

I. 0·5896 gram of the salt, dried at 100° and a vacuum over sulphuric acid, lost 0·0480 gram H_2O at 125°.

	Found.	Theory.
$2H_2O$	8·1	9·0

II. 0·5416 gram of the anhydrous salt gave 0·1152 gram of Na_2SO_4.

	Found.	Theory.
Na	6·89	6·81

Ammonium Salt.—This was prepared in the same way as the α-salt previously described. The first crystalline product, on twice recrystallising gave an almost colourless, silky product, which was exactly similar to the α-salt in appearance.

The rotation in a 20-dec. tube for an aqueous solution was found to be $\alpha = 7° 40''$.

$$\therefore [\alpha]_D = +82°; \text{ the } \alpha\text{-salt gave } [\alpha]_D = +87°.$$

Estimation of Sulphur by Carius' Method.

0·3171 gram substance gave 0·2324 gram $BaSO_4$.

	Found.	Theory.
S.............	10·06	9·75

From the rotation values, this salt appears to be practically identical with the α-salt.

The *potassium salt* of the β-acid was also prepared, but, owing to its deliquescent nature, was not fully examined.

Preparation of Chlorocamphor.

The two isomeric chlorocamphors of P. Cazeneuve (*Compt. rend.*, **95**, 1358) were obtained by his method of chlorinating camphor in alcoholic solution. His process may, however, be improved by distilling the product under diminished pressure before proceeding to separate the two isomers. In this way, the unaltered camphor was removed by heating the mixture at 130° under a pressure of 5 mm. for an hour, when 40 grams of unaltered camphor was recovered. The rest boiled at 135°, and nearly the whole distilled over between 135° and 140°. This fraction was then treated with spirit and fractionally crystallised in the same way as in the case of the corresponding bromo-derivatives.

The isomeric chlorocamphors are in every way analogous to the bromo-compounds, and two fairly pure specimens of the α- and β-isomers were ultimately obtained and employed in these researches.

An oil (as in the case of the bromo-derivatives) was also obtained; it is probably a crude di-substituted chlorocamphor containing some β-chlorocamphor in solution.

Sulphonation of α- and β-Chlorocamphor.

The sulphonation was carried out in exactly the same way as in the case of the bromo-compounds, and the crude barium salts were identical in appearance and properties.

The barium salt of the α-sulphonic acid, when treated with the calculated quantity of potassium carbonate, gave a syrupy product which was dehydrated at 120°. 25 grams of α-chlorocamphor gave 46 grams of the anhydrous potassium salt, which is equivalent to a yield of 90 per cent.

On analysis, the potassium salt gave the following results :—

I. 0·3240 gram substance gave 0·0886 gram K_2SO.

II. 0·1820 gram substance gave 0·0858 gram AgCl by Carius' method.

	Found.	Theory.
K	12·24	12·70
Cl...............	11·64	11·65

Ammonium α-Chlorocamphorsulphonate.—10 grams of the barium salt were treated with ammonium sulphate as previously described. A crop of delicate, moss-like aggregations of crystals was ultimately obtained which blackened and decomposed at 200°.

I. 0·2112 gram substance gave 0·1367 gram AgCl by Carius' method.

	Found.	Theory.
Cl...............	16·00	16·04

This agrees with the formula $C_{10}H_{14}ClO{\cdot}SO_3NH_4$.

α-Chlorocamphorsulphonic Chloride, $C_{10}H_{14}OCl{\cdot}SO_2Cl$.

The acid chloride was obtained by the action of phosphorus pentachloride on the anhydrous potassium salt. It was extracted with chloroform, and this solution when evaporated in a vacuum left a black, tarry residue which eventually solidified to a microcrystalline, black solid.

0·2096 gram substance gave 0·25565 gram AgCl.

	Found.	Theory.
Cl...............	24·52	24·91

It reacted with aniline, ammonia, alcoholic ammonia, ammonium carbonate (solid), and piperidine similarly to the chloride of α-bromocamphorsulphonic acid.

The piperidine derivative, on recrystallisation from alcohol, was obtained in delicate little needles of a reddish-brown tinge, but, owing to its great solubility, its purification was both difficult and tedious.

The β-chlorosulphonic derivatives are quite comparable with those of their β-bromo-congeners; for example, the barium and potassium salts are extremely deliquescent. non-crystallisable substances. Again the ammonium salt of the α-chlorinated acid is easily crystallisable from alcohol or water, the corresponding β-chloro-salt, however, like its analogue the β-bromo-salt of ammonium, is deliquescent and non-crystalline; it may be kept over sulphuric acid in a vacuum for weeks without becoming solid and dry.

University Laboratory, Oxford.

LXXXIV.—*Eulyte and Dyslyte.* (*A Correction.*)

By Henry Bassett.

My attention has lately been called to two papers on eulyte, one by Ciamician and Zatti (*Gazzetta*, 1889, **19**, 263), and the other by A. Angeli (*Ber.*, 1891, 1303). These authors have apparently not consulted the previous original papers on the subject, as the latter attributes my formulæ for eulyte and dyslyte to Baup, who published no analyses, whilst Ciamician and Zatti, who confirm my formula for eulyte, have not succeeded in obtaining dyslyte.

I was therefore induced to go carefully through the analyses and notes of my old paper (this Journal, 1872, 25, 98), and, to my annoyance, discovered an error in the melting points, the corrections having been deducted from, instead of added to, the observed temperatures.

The true melting points are, for eulyte 102·8°, and for dyslyte 200·5°, instead of 99·5° and 189° respectively.

In the course of the year 1872, I prepared a further quantity of these substances, with the intention of examining any basic derivatives by reduction; I did not, however, obtain anything but large quantities of ammonia and very unpromising, tarry products. My final yield of crystallised products was as follows:—eulyte 30 grams, and dyslyte 1·3 grams, and a certain quantity of the oily substance which is invariably produced at the same time.

Remembering the difficulty I found in separating these substances, even when operating with what may be called somewhat large quantities, and observing that Ciamician and Zatti's percentages of carbon are in every case higher than the calculated number, contrary to what usually happens in carbon determinations; noting also the curious circumstance that the percentages of nitrogen and hydrogen as found by me in the two substances happen to be very nearly alike, it occurred to me to calculate the percentage of carbon in a mixture of eulyte and dyslyte in the proportions mentioned above.

This calculated percentage is 29·61, almost exactly Ciamician and Zatti's mean, which is 29·59, and it is difficult to avoid the obvious inference that they really had to do with a similar mixture.

I give below a comparative statement of the analyses of the two substances:—

Eulyte.

	Exp. mean (C. & Z.).	Exp. mean (H.B.).	Theory. $C_6H_6N_4O_7$.
C.	29·59	29 26	29·27
H.........	2·83	2·61	2·44*
N.........	22·68	22·60	22·76

Dyslyte.

	Exp. mean (H. B.).	Theory. $C_8H_6N_4O_6$.
C..............	37·80	37·80
H	2·50	2·36
N	21·97	22·05

Having some citraconic acid still remaining from my former work, I have quite recently made some further experiments, resulting in a much better method of preparation of the two substances in question, and which seems to be of sufficient interest for publication. Instead of using strong nitric acid, I dissolved the citraconic acid in its own weight of water, and then added 1½ times its weight of nitric acid (the ordinary pure acid of 1·42 sp. gr.) in successive small portions; the mixture being heated on a water-bath in a flask with a long tube ground into the neck, as I found an appreciable loss occurred without this precaution. After a time, a gentle evolution of carbonic acid began, and continued the whole time (about two days), with only slight indications of nitrous fumes.

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* In my original paper this number was erroneously given as 2·52; in the paper by Ciamician and Zatti, it is 2·46. The correct number is as stated above.

Under these circumstances, it became obvious that eulyte and dyslyte are really products of the action of nitric acid on mesaconic acid, as after a certain point large quantities of this acid crystallised out on cooling, while beyond this point, that is, on further heating with more nitric acid, the mesaconic acid gradually diminished, and oily drops appeared, increasing more and more until finally no mesaconic acid separated on cooling. An experiment with crystallised mesaconic acid gave in fact a considerably greater yield of the oily product than that obtained from citraconic acid.

I may here mention that itaconic acid is much more violently acted on by nitric acid, the solution becoming dark red, with evolution of large quantities of gas having the characteristic repulsive smell of a carbamine. It gives no mesaconic acid, as is well known, and no eulyte.

When the action came to an end, the oily globules remained fluid for a day or two, but, on agitation, a very minute quantity of crystalline needles separated from the mother liquor, which on coming in contact with the oil caused it to solidify in a few minutes. The acid liquid was poured off and evaporated to a small bulk, when a strong action began, and lasted for some minutes, after which the addition of water caused the separation of a little more oil.

I must not omit to mention that the acid liquid contains a considerable amount of acetic acid, besides a certain quantity of oxalic and mesaconic acids, and a gummy acid giving a very soluble calcium salt.

The solidified mass, after washing with water till practically free from acid, was treated with a little cold alcohol to remove the greater part of the fluid oil, boiled for a few minutes with alcohol of about 80 per cent. in quantity insufficient to dissolve the whole, and the solution poured off and allowed to crystallise. The product thus obtained was again boiled with an insufficient quantity of alcohol, and so on. The less soluble portions dissolved with difficulty in boiling alcohol, and, on cooling, deposited very fine, transparent needles of dyslyte, totally unlike the thick, prismatic crystals of eulyte. By this method of fractional solution and crystallisation, I obtained from 77 grams of citraconic acid 4·1 grams of eulyte and 0·35 gram of dyslyte, the yield of the two substances together being decidedly greater than when strong nitric acid is used, and the proportion of dyslyte being more than doubled. The quantity of the fluid oil is also greater, doubtless owing to the use of a condensing tube.

Having neither time nor facilities for the further study of these remarkable substances, I shall look forward with much interest for future researches by Professor Ciamician and his friends as to their constitution, the elucidation of which would undoubtedly be of considerable theoretical importance.

LXXXV.—*The Magnetic Rotatory Power of Solutions of Ammonium and Sodium Salts of some of the Fatty Acids.*

By W. H. PERKIN, Ph.D., F.R.S.

LAST January, a paper on "Magnetic Rotation," by Professor Ostwald, was read before this Society (this vol., p. 198), in which he referred to the results I had obtained on the rotatory power of sulphuric and nitric acids of different strengths (Trans., 1886, **49**, 752, and 1889, **55**, 681), and on the solutions of ammonium salts (Trans., 1889, **55**, 742) and of saline solution, a preliminary account of which I brought before the Society 12 months since (Proc., 1890–91, 141). These results he considers are in full accordance with the dissociation theory of Arrhenius, whether the effect of solution causes an increase in rotatory power as in the case of the haloïd salts, or a decrease, as in the case of the oxygen acids and their salts. He also refers to the cases in which aqueous solutions possess an additive character only, such as alcohol, ammonia, and formic, acetic, and propionic acids, remarking that all of these are much poorer conductors of electricity than the strong acids and bases, and that since salts formed from weak acids are as good conductors as those formed from strong ones, we may expect with them also marked deviations from the calculated values, and he further remarked that as no observations have, up to the present, been made with such compounds, it would be of interest to investigate some of these salts, such as ammonium formate and acetate.

In his valuable work on Solution, p. 279 (English edition, 1891), after taking exception to my remarks in reference to solutions of some ammonium salts (Trans., 1889, **55**, 743) that the only explanation I can find for these remarkable results is that these salts, when in solution, are almost entirely dissociated into their acids and bases, he observes, "there can be no doubt that such salts as ammonium formate, &c., when in aqueous solution, would show molecular rotations which would not be the sums of the rotations of the components of the salts, but the rotations must be the sums of those of the components if Perkin's view is correct."* It would be easy then to make a crucial experiment, which should decide between the two theories. These observations induced me to direct my attention to the examination of some of the salts of the fatty acids, to see if the above observations were confirmed or not by experiment. The following are the results obtained:—

Solution I.

Ammonium Formate, $\mathrm{Am\overline{Fo} + 3\,OH_2}$.

The density determinations gave—

d 15°/15° 1·1275. *d* 25°/25° 1·1256.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	14·5°	1·1054	6·371
	14·5	1·1024	6·353
	14·5	1·1054	6·371
	14·5	1·1047	6·366
	17·5	1·1029	6·362
	17·5	1·1037	6·365
	18·5	1·1045	6·371
	18·5	1·0967	6·326
	19·0	1·1032	6·364
	19·0	1·1047	6·372
	19·0	1·1036	6·366
	19·5	1·1035	6·367
	19·5	1·1028	6·362
Average	17·4	1·1034	6·363
	Less 3 mols. OH_2		3·000
			3·363

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* This would only be the case if the salts were perfectly dissociated, otherwise the rotation would be less.

Solution II.

Ammonium Formate, $\mathrm{Am\overline{Fo}} + 8{\cdot}78\ \mathrm{OH_2}$.

The density determinations gave—

$d\,15°/15°$ 1·0732. $d\,25°/25°$ 1·0719.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
17·5°	1·0631	12·168
17·5	1·0631	12·168
17·5	1·0631	12·168
19·0	1·0683	12·229
19·0	1·0671	12·216
19·0	1·0642	12·182
19·0	1·0686	12·233
19·0	1·0619	12·156
19·0	1·0645	12·186
19·0	1·0631	12·169
19·0	1·0660	12·203
19·0	1·0638	12·178
Average 18·6	1·0644	12·174
Less 8·78 mols. OH_2		8·780
		3·394

Solution III.

Ammonium Formate, $\mathrm{Am\overline{Fo}} + 10\ \mathrm{OH_2}$.

The density determinations gave—

$d\,15°/15°$ 1·0674. $d\,25°/25°$ 1·0662.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
15·0°	1·0571	13·371
15·0	1·0523	13·310
15·0	1·0523	13·310
15·0	1·0550	13·344
17·5	1·0559	13·360
17·5	1·0541	13·337
17·5	1·0534	13·327
17·5	1·0529	13·322
17·5	1·0526	13·322
Average 16·4	1·0539	13·333
Less 10 mols. OH_2		10·000
		3·333

Solution I.

Ammonium Acetate, $AmAc$ + 4·75 OH_2.

The density determinations gave—

d 15°/15° 1·0841. d 25°/25° 1·0824.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
15·0°	1·0832	9·019
15·0	1·0728	8·933
15·5	1·0824	9·014
15·5	1·0824	9·014
18·0	1·0777	8·979
18·0	1·0837	9·029
18·0	1·0782	8·983
18·0	1·0797	8·995
Average 16·6	1·0800	8·996
Less 4·75 mols. OH_2..........		4·750
		4·246

Solution II.

Ammonium Acetate, $AmAc$ + 13·13 OH_2.

The density determinations gave—

d 15°/15° 1·0489. d 25°/25° 1·0480.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
18·0°	1·0487	17·409
18·0	1·0453	17·352
18·0	1·0445	17·339
18·0	1·0468	17·376
18·5	1·0475	17·390
18·5	1·0457	17·361
18·5	1·0482	17·402
18·5	1·0475	17·390
Average 18·2	1·0468	17·377
Less 13·13 mols. OH_2..........		13·130
		4·247

Solution I.

Ammonium Propionate, $\mathrm{Am\overline{Pr}} + 2{\cdot}86\ \mathrm{OH_2}$.

This solution was prepared by mixing the theoretical quantities of strong aqueous ammonia and propionic acid.

The density determinations gave—

d 15°/15° 1·0755. *d* 25°/25° 1·0726.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
17·0°	1·1034	8·109
17·0	1·1044	8·135
17·0	1·1007	8·108
17·0	1·1044	8·135
19·5	1·0995	8·105
19·5	1·1010	8·116
19·5	1·0988	8·090
Average 18·0	1·1018	8·115
Less 2·86 mols. $\mathrm{OH_2}$…………		2·860
		5·255

Solution II.

Ammonium Propionate, $\mathrm{Am\overline{Pr}} + 10{\cdot}29\ \mathrm{OH_2}$

The density determinations gave—

d 15°/15° 1·0535. *d* 25°/25° 1·0516.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
19·0°	1·0634	15·497
19·0	1·0671	15·552
19·0	1·0665	15·543
19·0	1·0650	15·521
19·0	1·0671	15·552
19·5	1·0695	15·587
19·5	1·0709	15·608
19·5	1·0683	15·569
19·5	1·0671	15·552
Average 19·2	1·0672	15·533
Less 10·29 mols. $\mathrm{OH_2}$…………		10·290
		5·263

Solution I.

Sodium Formate, $\mathrm{Na\overline{Fo}} + 5{\cdot}40\ \mathrm{OH_2}$.

The density determinations gave—

d 15°/15° 1·2905. *d* 25°/25° 1·2869.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
18·0°	1·0876	7·744
18·0	1·0894	7·757
18·0	1·0894	7·757
18·0	1·0921	7·775
19·5	1·0920	7·775
19·5	1·0920	7·775
19·5	1·0913	7·770
19·5	1·0893	7·756
Average 18·75	1·0904	7·764
Less 5·4 mols. $\mathrm{OH_2}$		5·400
		2·364

Solution II.

Sodium Formate, $\mathrm{Na\overline{Fo}} + 12{\cdot}54\ \mathrm{OH_2}$.

The density determinations gave—

d 15°/15° 1·1551. *d* 25°/25° 1·1526.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
15·0°	1·0501	14 835
15·0	1·0542	14·893
15 0	1·0572	14·935
15·0	1·0553	14·908
15·0	1·0595	14·967
18·0	1·0529	14·883
18·0	1·0506	14·852
18·2	1·0498	14·825
18·2	1·0498	14·825
18·2	1·0503	14·850
18·2	0·0503	14·846
18·2	1·0495	14·835
Average 16·8	1·0525	14·871
Less 12·54 $\mathrm{OH_2}$		12·540
		2 331

Sodium Acetate, $\mathrm{Na\overline{Ac}} + 11{\cdot}23\ \mathrm{OH_2}$.

The density determinations gave—

d 15°/15° 1·1578. *d* 25°/25° 1·1553.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
13·0°	1·0642	14·504
13·0	1·0649	14·548
13·0	1·0597	14·443
13·0	1·0627	14·484
13·5	1·0678	14·559
13·5	1·0683	14·565
13·5	1·0693	14·579
13·5	1·0671	14·549
16·2	1·0665	14·546
16·2	1·0590	14·444
16·2	1·0590	14·444
16·2	1·0620	14·485
16·2	1·0604	14·465
19·0	1·0609	14·480
19·0	1·0657	14·546
19·0	1·0654	14·541
Average 15·2	1·0639	14·511
Less 11·23 mols. $\mathrm{OH_2}$		11·230
		3·281

Sodium Propionate, $\mathrm{Na\overline{Pr}} + 7\ \mathrm{OH_2}$.

The density determinations gave—

d 15°/15° 1·1958. *d* 25°/25° 1·1913.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
15·0°	1·0876	11·260
15·0	1·0943	11·329
15·0	1·0876	11·260
15·0	1·0950	11·337
15·5	1·0994	11·343
15·5	1·0980	11·328
15·5	1·0950	11·298
Average 15·2	1·0938	11·308
Less 7 mols. $\mathrm{OH_2}$.............		7·000
		4·308

Sodium Butyrate. $Na\overline{Bu} + 6{\cdot}81\ OH_2$.

The density determinations gave—

$d\,15^\circ/15^\circ$ 1·1688. $d\,25^\circ/25^\circ$ 1·1646.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
18·0°	1·0951	12·121
18·0	1·0973	12·145
18·0	1·0969	12·141
18·0	1·0996	12·170
19·0	1·0957	12·132
19·0	1·0967	12·143
19·0	1·0972	12·148
19·0	1·0964	12·140
Average 18·5	1·0968	12·142
Less 6·81 mols. OH_2..........		6·81
		5·332

The following table gives the results obtained, side by side with their averages:—

Salt.	Water.	Mol. rotation.	Average mol. rotation.
	mols.		
Ammonium formate	+8·00	3·363	—
" "	+8·78	3·394	—
" "	+10·00	3·333	3·363
" acetate.............	+4·75	4·246	—
" "	+13·13	4·247	4·247
" propionate...	+2·86	5·255	—
" "	+10·26	5·263	5·259
Sodium formate.................	+5·40	2·364	—
" "	+12·54	2·331	2·347
" acetate	+11·23	3·281	3·281
" propionate	+7·00	4·308	4·308
" butyrate	+6·81	5·332	5·332

From these results it is seen that the rotatory powers of the ammonium salts do not vary with different degrees of dilution, and there can be but little doubt that this is also true of the sodium salts, because sodium formate shows no difference in this respect in solutions of varying strengths.

On comparing the results obtained with the ammonium salts with the rotations of the base and acids, we get the following results:—

	CH_2O_2 = 1·671	$C_2H_4O_2$ = 2·525	$C_3H_6O_2$ = 3·462
	NH_3 = 1·818	NH_3 = 1·818	NH_3 = 1·818
	3·489	4·343	5·280
Found for ammonium salts	3·363	4·247	5·259
Difference	0·126	0·096	0·021

This shows that the rotations of the salts are a little less than the sums of the acids and base; this is what might be expected, as reduction always takes place on combination. The question in this case is, how much reduction should we expect? We can get an answer which will not be far from the truth by considering the formation of the corresponding ethereal salts—

	CH_2O_2 = 1·671	$C_2H_4O_2$ = 2·525	$C_3H_6O_2$ = 3·462
	C_2H_4 = 2·046	C_2H_4 = 2·046	C_2H_4 = 2·046
	3·717	4·571	5·508
Found for ethereal salts..........	3·561	4·462	5·452
Difference	0·153	0·109	0·052

These differences correspond closely with those of the ammonium salts, being only a very little larger.

Another comparison may be made, namely, between the rotations of these salts and those of the ethereal salts—

	Mol. rotation.	Diff.		Mol. rotation.	Diff.
CHO_2NH_4	3·363	0·874	CHO_2Et....	3·561	0·898
$C_2H_3O_2NH_4$ ...	4·247	1·012	$C_2H_3O_2Et$ ..	4·462	0·990
$C_3H_5O_2NH_4$ ...	5·259		$C_3H_5O_2Et$ ..	5·452	

Here again the analogy is very close. Therefore, as these salts when in solution correspond in their formation and relationships to the ethers which are anhydrous, these results would indicate that the rotations obtained for them when in solution are practically the same as those which they possess when in the dry state. As, however, the first set of comparisons with the ethers shows a slightly smaller set of differences, and the numbers approach more nearly to the sums of the rotations of their components, it may be that small amounts of these salts when in solution do dissociate into their acids and base; at any rate, they do not bear out Professor Ostwald's anticipations of marked deviations from the calculated values.

In the case of the sodium salts, we are not in a position to form such good conclusions from the results, because we do not know the true value of sodium; but we can compare the relationships which exist between them and the ethers—

	Mol. rotation.	Diff.		Mol. rotation.	Diff.
CHO_2Na......	2·341	0·940	CHO_2Et ...	3·564	0·898
$C_2H_3O_2Na$.....	3·281	1·027	$C_2H_3O_2Et$ ..	4·462	0·990
$C_3H_5O_2Na$.....	4·308	1·023	$C_3H_5O_2Et$ ..	5·452	1·025
$C_4H_7O_2Na$.....	5·331		$C_4H_7O_2Et$ ..	6·477	

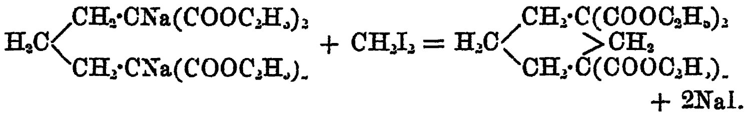
These differences are nearly as close to each other as in the case of the ammonium salts, so that whatever influence water may have on these salts, if any, it evidently acts to the same extent on all of them; but whether these numbers show the true value of these salts, it is impossible to say at present. I have determined the rotatory power of rock salt, and this gives a much higher value for sodium than any of the salts of oxygenated acids yet examined do; but it is just possible that the value of a metal may be so influenced when replacing hydrogen in an oxygenated acid as to give lower numbers than when in union with a halogen, and I am inclined to think this will be found to be the case. To get information regarding the relationship of metals to their salts, I am engaged with the examination of the magnetic rotatory powers of some of the organo-metallic compounds, and the salts formed from the metals they contain. I hope also to examine some of the ammonium and other salts of the polybasic organic acids.

LXXXVI.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

New Synthesis of the Hexamethylenedicarboxylic Acids.

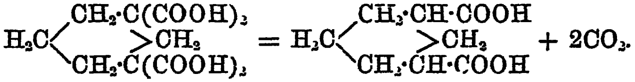
By W. H. PERKIN, Jun., Ph.D., F.R.S., and BERTRAM PRENTICE.

IN the last number of this Journal (p. 798), it was shown that the sodium compound of ethyl pentanetetracarboxylate reacts with methylene iodide in alcoholic solution at 100°, with formation of ethyl hexamethylenetetracarboxylate, thus:—



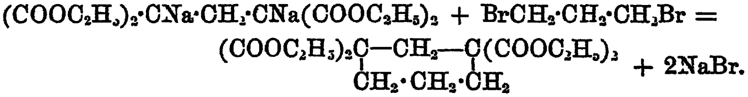
$$H_2C\left\langle\begin{array}{l}CH_2\cdot CNa(COOC_2H_5)_2\\ CH_2\cdot CNa(COOC_2H_5)_2\end{array}\right. + CH_2I_2 = H_2C\left\langle\begin{array}{l}CH_2\cdot C(COOC_2H_5)_2\\ \qquad >CH_2\\ CH_2\cdot C(COOC_2H_5)_2\end{array}\right. + 2NaI.$$

On hydrolysis, this ethereal salt yields the corresponding hexamethylenetetracarboxylic acid, and the latter, when heated at 200—220°, is decomposed with elimination of 2 mols. of CO_2. and formation of Γ^{cis} and $\Gamma^{cistrans}$ hexamethylenemetadicarboxylic acids:—



$$H_2C\left\langle\begin{array}{l}CH_2\cdot C(COOH)_2\\ \qquad >CH_2\\ CH_2\cdot C(COOH)_2\end{array}\right. = H_2C\left\langle\begin{array}{l}CH_2\cdot CH\cdot COOH\\ \qquad >CH_2\\ CH_2\cdot CH\cdot COOH\end{array}\right. + 2CO_2.$$

As the amount of these interesting acids obtained by this method is small, numerous experiments were made, under very varying conditions, with the object of improving the yield, but without success. It then seemed probable that the same ethyl hexamethylenetetracarboxylate should result from the action of trimethylene bromide on the disodium compound of ethyl propanetetracarboxylate, thus:—



$$(COOC_2H_5)_2\cdot CNa\cdot CH_2\cdot CNa(COOC_2H_5)_2 + BrCH_2\cdot CH_2\cdot CH_2Br =$$
$$\begin{array}{c}(COOC_2H_5)_2C—CH_2—C(COOC_2H_5)_2\\ |\qquad\qquad\qquad |\\ CH_2\cdot CH_2\cdot CH_2\end{array} + 2NaBr.$$

On making the experiment, it was found that a considerable quantity of the ethereal salt may be prepared in this way, but the yield obtained, though better than that from ethyl pentanetetracarboxylate, is far from good, and does not appear to be more than 10—12 per cent. of theoretical.

Preparation of Ethyl Propanetetracarboxylate, $(COOC_2H_5)_2CH\cdot CH_2\cdot CH(COOC_2H_5)_2$, *and of Glutaric Acid.*

Ethyl propanetetracarboxylate was first prepared by Conrad and Guthzeit (*Annalen*, **222**, 253), afterwards by W. H. Perkin, jun. (*Ber.*, **19**, 1056), by the condensation of ethyl malonate with formaldehyde:

$$2(COOC_2H_5)_2CH_2 + CH_2O = (COOC_2H_5)_2CH\cdot CH_2\cdot CH(COOC_2H_5)_2 + H_2O.$$

Subsequently, Guthzeit and Dressel (*Annalen*, **256**, 171) obtained the same substance by treating the sodium compound of ethyl malonate with methylene iodide, thus:—

$$2(COOC_2H_5)_2CHNa + CH_2I_2 = (COOC_2H_5)_2CH\cdot CH_2\cdot CH(COOC_2H_5)_2 + 2NaI.$$

This method gives a yield of 84 per cent. of the theoretical, and is, therefore, the most convenient method of preparation.

As, however, methylene iodide is an expensive substance, it occurred to us that it would be a great advantage if we could employ the cheaper methylene chloride in its place, and we, therefore, instituted a number of experiments on the action of methylene chloride on the sodium compound of ethyl malonate. 64 grams of ethyl malonate was dissolved in a solution of 9·2 grams of sodium in absolute alcohol, 17 grams of methylene chloride added, and the mixture heated in soda-water bottles at 100° for two hours; the product was then heated on a water-bath till free from alcohol, the residue mixed with water, and extracted three times with ether. During this operation, beautiful, yellow crystals separated from the ethereal solution; they contain sodium, and consist apparently of the sodium compound of a somewhat complicated ethereal salt; this substance, which seems to have very interesting properties, is at present under examination. The filtrate from this sodium compound, after drying over calcium chloride and evaporating the ether, deposited a thick oil, which was purified by fractional distillation under reduced pressure, and thus separated into unchanged ethyl malonate, and a substance boiling at 230—240° (80 mm.), which, after refractionation, boiled constantly at 234—236° (80 mm.), and was found to consist of pure ethyl propanetetracarboxylate.

0·2016 gram substance gave 0·1354 gram H_2O and 0·4020 gram CO_2.

	Theory. $C_{15}H_{24}O_8$.	Found.
C	54·21 per cent.	54·35 per cent.
H	7·23 „	7·46 „
O	38·55 „	38·19 „

The yield obtained was about 60 per cent. of the theoretical, without taking the recovered ethyl malonate into account.

The action of methylene chloride on the sodium compound of ethyl malonate has been already investigated by S. Tanatar (*Chem. Centralblatt*, 1891, i, 21, 22), but his results differ entirely from those described above, as he makes no mention of having obtained an ethereal salt, $C_{15}H_{24}O_8$. On this account it seemed necessary to prove that the ethereal salt, $C_{15}H_{24}O_8$, obtained by this reaction, really was ethyl propanetetracarboxylate before employing it for synthetical experiments. This is readily done by converting it into the corresponding tetracarboxylic acid, and then decomposing this by heating it at 200°, when glutaric acid results (compare W. H. Perkin, jun., Guthzeit and Dressel, *loc. cit.*).

$$(COOH)_2CH{\cdot}CH_2{\cdot}CH(COOH)_2 = COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + 2CO_2.$$

30 grams of the pure ethyl salt, $C_{15}H_{24}O_8$, was dissolved in methyl alcohol, mixed with a solution of 25 grams of potassium hydrate in methyl alcohol, and the whole heated for three hours on a water-bath, in a flask connected with a reflux apparatus. The product was then mixed with water, vigorously boiled till free from alcohol, evaporated to a small bulk, acidified with hydrochloric acid, and extracted 10 times with pure ether. The ethereal solution was dried over calcium chloride, evaporated, and the residual, yellowish, semi-solid mass heated at 200—220° until the evolution of carbonic anhydride had entirely ceased.

In order to purify the crude acid thus obtained, the residual dark-brown syrup was dissolved in 10 times its weight of absolute alcohol, the solution mixed with 1/5th of the quantity of concentrated sulphuric acid, heated in a reflux apparatus for two hours, and the ethereal salt isolated by pouring the product into water and extracting with ether. The ethereal solution was well washed with water, dried over calcium chloride, evaporated, and the crude ethyl salt purified by fractional distillation. In this way a colourless oil was obtained, which boiled constantly at 234°, and showed all the properties of ethyl glutarate. Analysis :—

0·1104 gram substance gave 0·0864 gram H_2O and 0·2321 gram CO_2.

	Theory. $COOC_2H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_2H_5$.	Found.
C	57·44 per cent.	57·34 per cent.
H	8·51 „	8·68 „
O	34·05 „	33·98 „

The pure ethereal salt was hydrolysed by boiling with an excess of alcoholic potash for two hours, the solution mixed with water, boiled until free from alcohol, acidified with hydrochloric acid, and extracted five times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a crystalline cake of almost pure glutaric acid; this was washed with ether, dried on a porous plate over sulphuric acid, under reduced pressure, and then at 80°.

The acid melted at 97—98°, and on analysis gave numbers agreeing with those required for glutaric acid.

0·1702 gram substance gave 0·0950 gram H_2O and 0·2836 gram CO_2.

	Theory. $C_5H_8O_4$.	Found.
C	45·45 per cent.	45·48 per cent.
H	6·06 „	6·20 „
O	48·48 „	48·32 „

The formation of this acid proves that the substance $C_{15}H_{24}O_{8}$, obtained by the action of methylene chloride on the sodium compound of ethyl malonate, is in reality ethyl propanetetracarboxylate, $(COOC_2H_5)_2CH{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2$.

The method of preparation of glutaric acid given above is probably the simplest and cheapest way of preparing this important substance, and, with this object in view, it would not be necessary to purify the ethyl propanetetracarboxylate by fractionation, the crude product of the action of methylene chloride on the sodium compound of ethyl malonate, might be freed from unchanged ethyl malonate by distillation in a current of steam, and the residual oil at once hydrolysed and treated as above.

Action of Trimethylene Bromide on the Disodium Compound of Ethyl Propanetetracarboxylate. Formation of Hexamethylenetetracarboxylic Acid.

In carrying out this synthesis, 70 grams of pure ethyl propanetetracarboxylate was mixed with a solution of 9·7 grams of sodium in 120 grams of absolute alcohol, 43 grams of trimethylene bromide added, and the whole heated gently in a flask connected with a reflux apparatus. In a short time, the temperature rose rapidly, a vigorous reaction set in, and, after boiling for about one hour, the decomposition was completed. The product was gently evaporated till free from alcohol, mixed with water, extracted two or three times with ether, the ethereal solution evaporated, and the residual oil (78 grams) hydrolysed by boiling with 1½ times the calculated quantity of alcoholic potash for three hours. After mixing with water, the alkaline solution was boiled until free from alcohol, evaporated to a small bulk, acidified with hydrochloric acid, and extracted 25 times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating to a small bulk, deposited, on standing, a quantity of a white, crystalline substance; this was collected, washed with ether, and recrystallised from warm water.

In this way, beautiful, colourless, glistening crystals were obtained, which, on analysis, proved to be pure hexamethylenetetracarboxylic acid:—

0·1418 gram substance gave 0·0620 gram H_2O and 0·2400 gram CO_2.

	Theory. $C_{10}H_{12}O_8$.	Found.
C	46·15 per cent.	46·15 per cent.
H	4·61 ,,	4·85 ,,
O	49·23 ,,	49·00 ,,

This substance, when rapidly heated, decomposed at 218—220°, and was in all respects identical with the hexamethylenetetracarboxylic acid previously obtained. A quantity of the pure acid was heated at 220° until the evolution of carbonic anhydride had ceased, and the resulting, almost colourless oil which consists of a mixture of Γ^{cis} and $\Gamma^{cistrans}$ hexamethylenemetadicarboxylic acids, digested with acetyl chloride, and thus converted into the anyhdride of the Γ^{cis} acid (this vol., pp. 812, 816). The solid, crystalline mass which remained after distilling off the excess of the acetyl chloride and the acetic acid was purified by spreading on a porous plate, and subsequent recrystallisation from a mixture of benzene and light petroleum.

The magnificent, glistening crystals thus obtained, after drying at 110°, melted at 187°, and consisted of the pure anhydride of Γ^{cis} hexamethylenemetadicarboxylic acid, as is shown by the following analyses:—

I. 0·1074 gram substance gave 0·0656 gram H_2O and 0·2451 gram CO_2.

II. 0·1599 gram substance gave 0·0958 gram H_2O and 0·3642 gram CO_2.

	Theory.	Found.	
	$C_8H_{10}O_3$.	I.	II.
C........	62·33 per cent.	62·24	62·11 per cent.
H.......	6·50 „	6·79	6·65 „
O........	31·17 „	30·97	31·24 „

This anhydride was further identified by conversion into Γ^{cis} hexamethylenemetadicarboxylic acid by boiling with water.

The ethereal mother liquors from which the hexamethylenetetracarboxylic acid had separated, as described above, were evaporated, the residue heated at 200—220° until the evolution of carbonic anhydride had ceased, and then converted into the methyl salt by means of methyl alcohol and sulphuric acid (*loc. cit.*, p. 806).

On fractioning this salt, a small amount of crude methyl hexamethylenedicarboxylate was obtained, boiling at 170—185° (60 mm.), together with considerable quantities of high and low boiling fractions; of these, the former were not examined; the latter appear to contain methyl glutarate, which must have been produced by the hydrolysis of some unchanged ethyl propanetetracarboxylate.

The yield of pure hexamethylenetetracarboxylic acid obtained in the above reaction from 140 grams of ethyl propanetetracarboxylate was about 13·5 grams, or about 12 per cent. of the theoretical. The amount of hexamethylenedicarboxylic acids obtained by the hydrolysis of the methyl salt has not yet been accurately determined, but it is approximately 4 grams.

Further experiments on these interesting acids are in progress.

LXXXVII.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

Benzoylacetic Acid and some of its Derivatives. Part V.

By W. H. Perkin, Jun., Ph.D., F.R.S., and James Stenhouse.

In previous investigations on ethyl benzoylacetate (Trans., 1884, **45**, 170; 1885, **47**, 240, 262; 1886, **49**, 154), it was shown that in its general behaviour it bore a very strong resemblance to ethyl acetoacetate. When treated with sodium ethylate, it forms a well-characterised sodium compound, $C_6H_5{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5$, which, by the action of alkyl haloïds, yields monalkyl substitution products. It still remained to be seen whether these alkyl derivatives, like the mono-substituted derivatives of ethyl acetoacetate, if again treated with sodium ethylate and alkyl haloïds, were capable of forming di-substitution products.

Numerous experiments were made on this subject, and, as a result, it was found that the mono-substituted ethyl benzoylacetates, such as ethyl methybenzoylacetate, $C_6H_5{\cdot}CO{\cdot}CH(CH_3){\cdot}COOC_2H_5$, when treated in the usual way in alcoholic solution with sodium ethylate and isobutyl iodide or benzyl chloride, were only to a small extent converted into di-substitution products, the bulk of the substance being hydrolysed by the sodium ethylate employed, with formation of benzoic and fatty acids, and, in the case of the benzyl chloride, a quantity of benzyl ethyl ether, $C_6H_5{\cdot}CH_2{\cdot}OC_2H_5$, was obtained.

Allyl iodide, on the other hand, converts the sodium compound of ethyl methylbenzoylacetate almost quantitatively into ethyl methylallylbenzoylacetate, $C_6H_5{\cdot}CO{\cdot}C(CH_3)(CH_2{\cdot}CH{:}CH_2){\cdot}COOC_2H_5$, and it is difficult to understand why allyl iodide should behave so differently from isobutyl iodide, unless indeed the former is more readily decomposed than the latter.

That the mono-substituted derivatives of ethyl benzoylacetate are capable of forming sodium compounds is clearly shown by the fact that the ethereal solutions of these compounds dissolve sodium with evolution of hydrogen. The resulting ethereal solutions of the sodium compounds react only very slowly with alkyl haloïds, although, on the addition of an acid chloride, separation of sodium chloride at once takes place.

Thus, the sodium compound of ethyl methylbenzoylacetate is readily acted on by benzoyl chloride with formation of ethyl methyldibenzoylacetate:—

$$C_6H_5\cdot CO\cdot CNa(CH_3)\cdot COOC_2H_5 + C_6H_5\cdot COCl = (C_6H_5\cdot CO)_2C(CH_3)\cdot C\,OOC_2H_5 + NaCl$$

The conclusion which may be drawn from these experiments is that ethyl benzoylacetate differs from ethyl acetoacetate in this respect, that, unlike the latter, it only with difficulty yields di-substitution products; it is, however, possible that under conditions other than those employed in this investigation, these di-substituted products may be more readily obtained, and experiments on this point are in progress.

The substance described in a previous paper (Trans., 1884, **45**, 181) as ethyl diethylbenzoylacetate, $C_6H_5\cdot CO\cdot C(C_2H_5)_2\cdot COOC_2H_5$, is very probably a mixture of this substance with considerable quantities of ethyl ethylbenzoylacetate, $C_6H_5\cdot CO\cdot CH(C_2H_5)\cdot COOC_2H_5$, a supposition which is borne out by the analytical numbers obtained in a subsequent examination of this product.

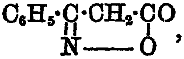
In the course of this investigation, we have taken the opportunity of correcting some errors which had crept into the previous work on the subject; we have also prepared a number of new and interesting compounds, and, before entering into experimental details, it will be well to give a brief account of the results obtained.

When the sodium compound of ethyl benzoylacetate is treated in ethereal solution with benzoyl chloride, ethyl dibenzoylacetate is produced:—

$$C_6H_5\cdot CO\cdot CHNa\cdot COOC_2H_5 + C_6H_5\cdot COCl = (C_6H_5\cdot CO)_2CH\cdot COOC_2H_5 + NaCl.$$

This interesting compound, which was previously described as an oil, is crystalline, and melts at 112°; on hydrolysis, it yields the corresponding dibenzoylacetic acid without decomposition.

Ethyl methyldibenzoylacetate, $(C_6H_5\cdot CO)_2C(CH_3)\cdot COOC_2H_5$ (see above), is, on the other hand, much less stable than ethyl dibenzoylacetate, as, when treated with alkalis, it is decomposed with formation of benzoic acid.

As dibenzoylacetic acid contains two carbonyl groups, it was thought probable that, when treated with hydroxylamine, it would yield a di-oxime, $[C_6H_5\cdot C(NOH)]_2CH\cdot COOH$; on making the experiment in alkaline solution, a substance, $C_9H_7NO_2$, was obtained, which, on examination, was found to be identical with *phenylisoxazolone*,  $\begin{array}{l}C_6H_5\cdot C\cdot CH_2\cdot CO\\ \quad\;\; N\text{——}O\end{array}$, which L. Claisen and W. Zedel (*Ber.*, **24**, 140) prepared by treating ethyl benzoylacetate with hydroxylamine in acetic acid solution. Under these circumstances, dibenzoylacetic acid is obviously decomposed with formation of benzoic and benzoylacetic acids, the latter then combining with hydroxylamine to form phenylisoxazolone.

In like manner, ethyl dibenzoylacetate and ethyl dibenzoylmethylacetate, when heated with phenylhydrazine, are decomposed with formation of benzoylphenylhydrazine, $C_6H_5 \cdot CO \cdot NH \cdot NH \cdot C_6H_5$.

Dibenzoylacetic acid is readily reduced by sodium amalgam in alkaline solution with formation of dihydroxydibenzylacetic acid, $[C_6H_5 \cdot CH(OH)]_2CH \cdot COOH$; but, at the same time, considerable quantities of β-phenyllactic acid, $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot COOH$, are produced, showing that a portion of the dibenzoylacetic acid, during the operation, had been decomposed into benzoylacetic and benzoic acids.

Ethyl ethylbenzoylacetate, when treated with sodium amalgam, yields α-ethyl-β-phenylhydroxypropionic acid,

$$C_6H_5 \cdot CH(OH) \cdot CH(C_2H_5) \cdot COOH$$

(m. p. 106—108°).

α-Methyl-β-phenylhydroxypropionic acid, when heated at a high temperature, is decomposed with formation of water, carbonic anhydride, and allylbenzene (methylstyrolene), $C_6H_5 \cdot CH{:}CH \cdot CH_3$.

Furfuraldehyde readily condenses with *ethyl benzoylacetate*, when a mixture of the two is digested with acetic anhydride, yielding ethyl furfuralbenzoylacetate, $C_6H_5 \cdot CO \cdot C({:}CH \cdot C_4H_3O) \cdot COOC_2H_5$, which melts at 68°.

Ethyl nitrosobenzoylacetate dissolves readily in potassium hydrate solution, and, on standing, is gradually decomposed with formation of nitrosoacetophenone, $C_6H_5 \cdot CO \cdot CH{:}NOH$, benzoic acid, and other products.

Ethyl benzylbenzoylacetate, $C_6H_5 \cdot CO \cdot CH(C_7H_7) \cdot COOC_2H_5$ (b. p. 265°, 80 mm.), is readily produced when the sodium compound of ethyl benzoylacetate is digested in alcoholic solution with benzyl chloride.

On hydrolysis, this ethereal salt is decomposed with formation of benzylacetophenone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, a crystalline substance which melts at 70° and, on treatment with hydroxylamine, yields an oxime, $C_6H_5 \cdot C(NOH) \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, melting at 80—81°.

Reduction with sodium, in moist ethereal solution, converts benzylacetophenone into diphenyl propyl alcohol,

$$C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot C_6H_5,$$

a thick, colourless oil which boils at 240° (70 mm.).

Experiments on the Formation of Di-substitution Derivatives of Ethyl Benzoylacetate.

Exp. I.—Ethyl methylbenzoylacetate (1 mol.) was digested in alcoholic solution with sodium ethylate (1 mol.) and excess of isobutyl iodide at 100° for two hours. The product was heated on a water-bath till free from alcohol, mixed with water, extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residual oil fractioned under reduced pressure. The greater part of the oil passed over between 160° and 170°, under a pressure of 225 mm., only a small quantity of an oil of high boiling point remaining in the retort.

On distillation under ordinary pressures, about three-quarters of the fraction 160—170° (225 mm.) passed over between 210—211°, and the distillate was found, on analysis, to consist of slightly impure ethyl benzoate.

0·1116 gram substance gave 0·0728 gram H_2O and 0·2950 gram CO_2.

	Theory. $C_6H_5{\cdot}COOC_2H_5$.	Found.
C	72·00 per cent.	72·92 per cent.
H	6·66 ,,	7·24 ,,
O	21·33 ,,	19·84 ,,

This crude ethereal salt gave, on hydrolysis, almost pure benzoic acid, which, after recrystallisation from water, melted at 120°.

Exp. II.—Ethyl methylbenzoylacetate (1 mol.) was digested in alcoholic solution with sodium ethylate (1 mol.) and excess of benzyl chloride. The product, isolated as above, was first distilled under reduced pressure and then fractioned under the ordinary pressure. Almost the whole passed over between 175° and 200°, leaving only a small residue, of a high boiling point, in the retort. On refractioning the oil boiling at 175—200°, a considerable quantity of a colourless distillate was obtained, boiling constantly at 185°; this, on examination, was found to consist of benzyl ethyl ether, $C_6H_5{\cdot}CH_2{\cdot}OC_2H_5$.

These and other experiments were repeated under various conditions, but in all cases the results were similar, except in the case of allyl iodide, which gives with the sodium compound of ethyl methylbenzoylacetate a very good yield of ethyl allylmethylbenzoylacetate (see next section).

Ethyl Allylmethylbenzoylacetate, $C_6H_5{\cdot}CO{\cdot}C(CH_2{\cdot}CH{:}CH_2)(CH_3){\cdot}COOC_2H_5$.

In order to prepare this ethereal salt, ethyl methylbenzoylacetate (1 mol.) was mixed with an alcoholic solution of sodium ethylate (1 mol.), an excess of allyl iodide added, and the whole heated on a water-bath for three hours in a flask connected with a reflux apparatus. After distilling off the alcohol, water was added, the product extracted twice with ether, the ethereal solution washed with water and a little sulphurous acid, dried over calcium chloride, evaporated, and the residual oil purified by repeated fractionation under reduced pressure (225 mm.). In this way a considerable quantity of a colourless oil was obtained, boiling at 243—245°, which, on analysis, gave the following numbers:—

0·1032 gram substance gave 0·0681 gram H_2O and 0·2774 gram CO_2.

	Theory. $C_{15}H_{18}O_3$.	Found.
C	73·17 per cent.	73·25 per cent.
H	7·32 „	7·36 „
O	19·51 „	19·39 „

Ethyl allylmethylbenzoylacetate is readily hydrolysed by boiling with alcoholic potassium hydrate solution; the principal products of the reaction are benzoic acid and an oily fatty acid of disagreeable odour, probably allylmethylacetic acid. A small quantity of a neutral substance is also formed, which boils approximately at 235°; this is presumably methylallylacetophenone, but it was not further examined.

Ethyl Dibenzoylacetate, $[C_6H_5{\cdot}CO]_2CH{\cdot}COOC_2H_5$.

The sodium compound of ethyl benzoylacetate reacts readily with benzoyl chloride with formation of ethyl dibenzoylacetate, thus:—

$$C_6H_5{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + C_6H_5{\cdot}COCl = (C_6H_5{\cdot}CO)_2CH{\cdot}COOC_2H + NaCl.$$

This ethereal salt can only be obtained in a crystalline condition if the ethyl benzoylacetate employed is very pure and free from acetophenone, and to the presence of the latter in considerable quantity in the ethyl benzoylacetate prepared from phenylpropiolic acid is due the fact that this substance was previously only obtained as an oil (Trans., 1885, **47**, 246).

In preparing large quantities of ethyl dibenzoylacetate, we have found the following method to give good results:—

25 grams of ethyl benzoylacetate is dissolved in 250 grams of pure dry ether, 3 grams of sodium, in the form of fine wire, added, and the whole allowed to stand until the sodium has completely dissolved, care being taken that the temperature does not rise above 25°. 19 grams of freshly distilled benzoyl chloride is then added slowly through a dropping funnel, the mixture allowed to stand for two hours, diluted with water, the ethereal solution separated, washed with water, and allowed to stand for 24 hours in a cool place. The crystalline mass which separates is collected, washed with ether, and dried on a porous plate over sulphuric acid under diminished

pressure. The beautifully crystalline, colourless powder thus obtained consists of pure ethyl dibenzoylacetate, as the following analyses show :—

0·1478 gram substance gave 0·0741 gram H_2O and 0·3970 gram CO_2.

0·1626 gram substance gave 0·0815 gram H_2O and 0·4351 gram CO_2.

	Theory.	Found.	
	$C_{18}H_{16}O_4$.	I.	II.
C	72 97 per cent.	73·25	72·97 per cent.
H	5 41 ,,	5·57	5·57 ,,
O.......	21·62 ,,	21·18	21·46 ,,

Ethyl dibenzoylacetate melts at 112°. It is sparingly soluble in ether, readily soluble in boiling alcohol, insoluble in water.

The ethereal mother liquors from the pure crystalline compound, on evaporation, deposit a yellow oil, which solidifies to a great extent on long standing over sulphuric acid in a vacuum. The crude pasty product thus obtained may be readily purified by contact with a porous plate until free from oily impurity, and subsequent trituration with absolute ether.

Ethyl dibenzoylacetate is readily hydrolysed by boiling with alcoholic potassium hydrate, with formation of dibenzoylacetic acid; the details of this operation, and the method of purification of the resulting acid, have been already given (Trans., 1885, **47**, 246).

Reduction of Dibenzoylacetic Acid. Formation of Dihydroxydibenzylacetic Acid, $[C_6H_5\cdot CH(OH)]_2CH\cdot COOH$, *and β-Phenyllactic Acid*, $C_6H_5\cdot CH(OH)\cdot CH_2\cdot COOH$.

Dibenzoylacetic acid is readily reduced by sodium amalgam in alkaline solution with formation of a mixture of dihydroxydibenzylacetic acid and β-phenyllactic acid.

The former acid is produced by the direct reduction of dibenzoylacetic acid, thus —

$$(C_6H_5\cdot CO)_2CH\cdot COOH + 2H_2 = [C_6H_5\cdot CH(OH)]_2CH\cdot COOH.$$

The latter acid results obviously from the reduction of benzoylacetic acid, which is produced by the decomposition of dibenzoylacetic acid in the presence of alkali, thus :—

$$(C_6H_5\cdot CO)_2CH\cdot COOH + H_2O = C_6H_5\cdot CO\cdot CH_2\cdot COOH + C_6H_5\cdot COOH.$$

$$C_6H_5\cdot CO\cdot CH_2\cdot COOH + H_2 = C_6H_5\cdot CH(OH)\cdot CH_2\cdot COOH.$$

Pure dibenzoylacetic acid was dissolved in a warm dilute solution of sodium carbonate, well cooled, and treated with a considerable excess of 2½ per cent. sodium amalgam in small quantities at a time. As the reduction proceeds, the solution becomes slightly turbid and smells of acetophenone, a small quantity of a dark-coloured sticky substance separates, which, however, owing to the small amount of material at our disposal, could not be obtained in a pure condition. The formation of a similar neutral reduction product was observed in experimenting on the action of sodium amalgam on ethyl benzoylacetate (Trans., 1885, **47**, 255); this was ultimately purified, and obtained in the form of colourless prisms melting at 102°; it seems very possible that this same substance is formed in both experiments, especially as the sticky substance from the reduction of dibenzoylacetic acid gives with alcoholic potash the intense magenta-red coloration, which is characteristic of the compound melting at 102°.

In order to isolate the principal products of the reduction of dibenzoylacetic acid, the alkaline solution was separated from the mercury by means of a separating funnel, acidified with dilute sulphuric acid, extracted several times with ether, and the ethereal solution dried over calcium chloride and evaporated. The yellowish oil thus obtained was digested with an excess of boiling baryta water for a short time, the excess of baryta removed by passing a rapid current of carbonic anhydride, the liquid filtered, and the colourless filtrate extracted twice with ether. In this way a small quantity of a neutral substance is removed; this will be referred to again later on.

The aqueous solution was then acidified with hydrochloric acid, extracted four times with ether, the ethereal solution dried over calcium chloride, evaporated, and the thick, almost colourless, oily residue allowed to stand over sulphuric acid under diminished pressure for several days. In order to remove the oily impurities, the resulting semi-solid mass was stirred up with successive small quantities of benzene, when a crystalline residue was left, which became quite colourless after repeated washing with benzene on a filter pump.

The crystals were then dissolved in a little hot water, the solution filtered, and allowed to cool slowly, and in this way beautiful, transparent, colourless needles were obtained, which after drying over sulphuric acid under diminished pressure, gave the following numbers on analysis:—

0·1526 gram substance gave 0·0808 gram H_2O and 0·3926 gram CO_2.

0·1586 gram substance gave 0·0848 gram H_2O and 0·4080 gram CO_2.

	Theory. $[C_6H_5 \cdot CH(OH)]_2CH \cdot COOH$.	Found. I.	 II.
C	70·59 per cent.	70·16	70·16 per cent.
H	5·88 „	5·89	5·94 „
O	23·53 „	23·95	23·90 „

Dihydroxydibenzylacetic acid melts at 188—190°, but not very sharply. It is readily soluble in hot water and alcohol, sparingly so in benzene and light petroleum.

The dissociation constant for the electrical conductivity of dihydroxydibenzylacetic acid at different concentrations was determined by Dr. Walker, who found $K = 0·0051$.

The basicity of this acid was determined by titration with a standard solution of potassium hydrate (1 c.c. = 0 00559 gram KOH).

0·1552 gram of the pure acid required for neutralisation 5 8 c.c. of the potassium hydrate solution = 0·0324 gram KOH.

A monobasic acid of the formula $C_{16}H_{16}O_4$ requires 0·0319 gram KOH.

The dilute solution of the potassium salt shows the following behaviour with reagents:—*Copper acetate*, a light-green precipitate, very sparingly soluble in water; *lead acetate*, a white, caseous precipitate, insoluble in water; *barium chloride*, no precipitate; *zinc acetate*, no precipitate.

On spontaneous evaporation, the benzene mother liquors from the above acid gradually deposit needle-shaped crystals; these were collected, washed with a little benzene, recrystallised from this solvent, and analysed with the following result:—

0·1501 gram substance gave 0·0812 gram H_2O and 0·3586 gram CO_2.

	Theory. $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot COOH$.	Found.
C	65·06 per cent.	65·16 per cent.
H.......	6·03 „	6·01 „
O	28·91 „	28·83 „

This substance melts at 91—93°, and is identical with the β-phenyllactic acid obtained by the reduction of benzoylacetic acid with sodium amalgam.

The silver salt was prepared by precipitating a neutral solution of the ammonium salt by silver nitrate. It gave the following results on analysis:—

0·2262 gram substance gave on ignition 0·0898 gram Ag = 39·61 per cent. Theory, $C_6H_5 \cdot CH(OH) \cdot CH_2COO$, Ag = 39·56 per cent.

The neutral oily substance obtained in the purification of the crude product of the action of sodium amalgam on dibenzoylacetic acid as described above solidified, almost completely, on standing. The crude product was spread on a porous plate and allowed to stand until the traces of oily impurity were entirely absorbed, and the colourless crystals analysed with the following result:—

0·0508 gram substance gave 0·0322 gram H_2O and 0·1478 gram CO_2.

	Theory. $C_{15}H_{16}O_2$.	Found.
C......	78·95 per cent.	79·33 per cent.
H.	7·01 „	7·04 „
O......	14·04 „	13·63 „

This substance, which melts at about 129°, is probably diphenyltrimethyleneglycol, $C_6H_5·CH(OH)·CH_2·CH(OH)·C_6H_5$, produced by the reduction of dibenzoylmethane, $C_6H_5·CO·CH_2·CO·C_6H_5$, which is one of the decomposition products of dibenzoylacetic acid.

Action of Hydroxylamine on Dibenzoylacetic Acid, and of Phenylhydrazine on Ethyl Dibenzoylacetate.

As dibenzoylacetic acid is a moderately stable substance, it seemed probable that, when treated with hydroxylamine in alkaline solution, it would yield a dioxime of the formula $[C_6H_5·C(NOH)]_2CH·COOH$, the examination of which might lead to very interesting results.

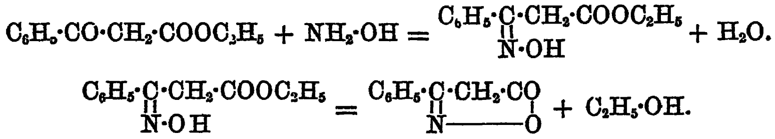
With the object of preparing this compound, pure dibenzoylacetic acid (1 mol.) was dissolved in methyl alcohol, mixed with a concentrated aqueous solution of hydroxylamine hydrochloride (3 mols.), an excess of potassium hydrate (6 mols.) added, and the whole allowed to stand for two days. The product was evaporated at a low temperature until free from methyl alcohol, mixed with water, acidified with dilute hydrochloric acid, and the crystalline precipitate which separated collected, washed with water, dried on a porous plate, and recrystallised twice from methyl alcohol. The beautiful crystalline compound thus obtained gave, on analysis, the following numbers:—

0·1320 gram substance gave 0·0586 gram H_2O and 0·3266 gram CO_2.

0·1648 gram substance gave 12·4 c.c. nitrogen; $t = 16°$; bar. = 732 mm.

	Theory. $C_9H_7NO_2$.	Found.
C.......	67·08 per cent.	67·47 per cent.
H.......	4·35 „	4·93 „
N.......	8·69 „	8·44

This substance melts at 146° with decomposition, and is identical with the phenylisoxazolon which L. Claisen and W. Zedel (*Ber.*, **24**, 140) obtained by treating ethyl benzoylacetate in acetic acid solution with hydroxylamine, thus:—



$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + NH_2{\cdot}OH = C_6H_5{\cdot}\underset{\substack{\| \\ N\cdot OH}}{C}{\cdot}CH_2{\cdot}COOC_2H_5 + H_2O.$$

$$C_6H_5{\cdot}\underset{\substack{\| \\ N\cdot OH}}{C}{\cdot}CH_2{\cdot}COOC_2H_5 = \begin{array}{l} C_6H_5{\cdot}C{\cdot}CH_2{\cdot}CO \\ \qquad\quad \| \qquad\qquad | \\ \qquad\quad N\text{———}O \end{array} + C_2H_5{\cdot}OH.$$

Phenylisoxazolon.

The formation of this compound is readily understood, if we suppose that dibenzoylacetic acid in alkaline solution is decomposed into benzoylacetic acid and benzoic acid. The former then reacts with hydroxylamine, forming phenylisoxazolon.

Experiments were then instituted on the action of phenylhydrazine on ethyl dibenzoylacetate. 2 grams of the pure substance was mixed with 2 grams of phenylhydrazine, and the mixture heated at 180° in a test-tube until all action had ceased. The product, which on cooling solidified, was powdered, washed with ether till free from oily impurity, dried on a porous plate, and recrystallised several times from benzene. The beautiful, white, silky substance thus obtained melted at 165—168°, and was found to consist of benzoylphenylhydrazine, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5$. Analysis:—

0·2116 gram substance gave 25·6 c.c. N; $t = 22°$; bar. = 740 mm.

	Theory. $C_{13}H_{12}N_2O$.	Found.
N........	13·21 per cent.	13·33 per cent.

In the formation of this substance, the ethyl dibenzoylacetate is evidently first hydrolysed with formation of benzoic and acetic acids, and the former then combines with the phenylhydrazine.

It is probable that, under other conditions, the direct product of the action of phenylhydrazine on ethyl dibenzoylacetate might be obtained, and further experiments on this subject are in progress.

Ethyl Dibenzoylmethylacetate, $(C_6H_5{\cdot}CO)_2C(CH_3){\cdot}COOC_2H_5$.

This interesting substance was obtained in the following way:—1·6 grams of sodium wire was suspended in pure dry ether, 15 grams of ethyl methylbenzoylacetate, $C_6H_5{\cdot}CO{\cdot}CH(CH_3){\cdot}COOC_2H_5$, added, the mixture allowed to stand until the sodium had entirely dissolved, and 12 grams of freshly distilled benzoyl chloride gradually added. After standing for two hours, water was added, the ethereal solution separated, washed repeatedly with dilute sodium carbonate solution to remove any excess of benzoyl chloride, dried over calcium chloride, evaporated, and the residual oil, after standing over sulphuric acid under diminished pressure, analysed with the following result:—

0·2102 gram substance gave 0·1134 gram H_2O and 0·5618 gram CO_2.

	Theory. $C_{19}H_{18}O_4$.	Found.
C	73·55 per cent.	72·89 per cent.
H	5·81 ,,	5·99 ,,
O	20·64 ,,	21·12 ,,

Ethyl dibenzoylmethylacetate is a thick, yellowish oil, which, even on long standing, does not solidify; it is readily hydrolysed by boiling with alcoholic potash, with formation of benzoic acid and a neutral substance which is probably phenyl ethyl ketone, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_3$, and all attempts to obtain the corresponding dibenzoylmethylacetic acid were fruitless. When ethyl dibenzoylmethylacetate is heated in a test-tube with phenylhydrazine at 180°, benzoylphenylhydrazine is produced. This substance, after repeated recrystallisation, melted at 165°, and gave the following results on analysis:—

0·2296 gram substance gave 2·64 c.c. N; $t = 15°$; bar. = 744 mm.
0·1630 ,, ,, 0·0836 gram H_2O and 0·4400 gram CO_2.

	Theory. $C_6H_5{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5$.	Found.
C......	73·58 per cent.	73·62 per cent.
H......	5·66 ,,	5·70 ,,
N......	13·20 ,,	13·18 ,,

Ethyl Benzylbenzoylacetate, $C_6H_5{\cdot}CO{\cdot}CH(C_7H_7){\cdot}COOC_2H_5$.

This ethereal salt is readily prepared by treating the sodium compound of ethyl benzoylacetate with benzyl chloride in alcoholic solution, thus:—

$$C_6H_5{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + C_7H_7Cl = C_6H_5{\cdot}CO{\cdot}CH(C_7H_7){\cdot}COOC_2H_5 + NaCl.$$

40 grams of ethyl benzoylacetate was dissolved in a solution of 5 grams of sodium in 50 grams of absolute alcohol, 27 grams of freshly-distilled benzyl chloride added, and the mixture heated in a reflux apparatus on a water-bath for two hours. The alcohol was then distilled off, water added, the product extracted three times with ether, the ethereal solution washed with water, dried over calcium chloride, evaporated, and the residual, yellowish oil purified by fractionation

under diminished pressure (80 mm.). After a considerable quantity of an oil of low boiling point had passed over, smelling strongly of benzyl ethyl ether, $C_6H_5{\cdot}CH_2{\cdot}OC_2H_5$, the thermometer rose rapidly to 265°, between which temperature and 270° a considerable quantity distilled.

The almost colourless oil thus obtained gave on analysis the following numbers :—

0·1617 gram substance gave 0·1075 gram H_2O and 0·4544 gram CO_2.

	Theory. $C_{18}H_{18}O_3$.	Found.
C	76·60 per cent.	76·64 per cent.
H	6·39 „	6·79 „
O	17·02 „	16·57 „

Ethyl benzylbenzoylacetate is a thick, slightly-yellowish oil, which does not solidify even on long standing; it resembles closely the corresponding methyl salt, prepared by Perkin and Colman (Trans., 1886, **49**, 155) from methyl benzoylacetate by treatment with sodium ethylate and benzyl chloride.

Hydrolysis of Ethyl Benzylbenzoylacetate. Formation of Benzylacetophenone, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$.

In order to examine the behaviour of ethyl benzylbenzoylacetate on hydrolysis, a quantity of this ethereal salt was dissolved in absolute alcohol, heated to boiling on a water-bath in a reflux apparatus, and then a dilute solution of potassium hydrate (3 mols.) added, drop by drop, from a dropping funnel; after digesting for one hour, the solution was allowed to cool; on standing for 24 hours, a crystalline substance separated, which was collected, washed with a little alcohol, recrystallised from this solvent, and the beautifully glistening, colourless plates thus obtained dried over sulphuric acid under reduced pressure, and analysed with the following result :—

0·1239 gram substance gave 0·0765 gram H_2O and 0·3882 gram CO_2.

	Theory. $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$.	Found.
C	85·71 per cent.	85·53 per cent.
H	6·66 „	6·86 „
O	7·62 „	7·61 „

Benzylacetophenone melts at 70°. It is readily soluble in hot alcohol, benzene, and light petroleum; it crystallises from its hot solution in methyl alcohol or light petroleum in beautiful, glistening needles.

The alkaline filtrate from the crystals of benzylacetophenone was boiled till free from alcohol, filtered, acidified with hydrochloric acid, and extracted with ether. In this way a small quantity of an acid was extracted, which, on evaporating and subsequent recrystallisation of the residue from water, was obtained in colourless needles melting at 120°, and possessing the properties of benzoic acid, and the aqueous mother liquors from the benzoic acid, contained small quantities of a second acid, presumably phenylpropionic acid. The yield of ketone obtained by the above method is very good, approximately 80 per cent. of the theory; the formation of this ketone by the hydrolysis of ethyl benzylbenzoylacetate may be represented thus:—

$$C_6H_5{\cdot}CO{\cdot}CH(C_7H_7){\cdot}COOC_2H_5 + 2KOH = \\ C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5 + K_2CO_3 + C_2H_5{\cdot}OH.$$

Oxime of Benzylacetophenone, $C_6H_5{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$.

This oxime was prepared by dissolving the pure ketone (2 grams) in methyl alcohol, adding an aqueous solution of 1·5 grams of hydroxylamine hydrochloride and an alcoholic solution of 3 grams of potassium hydrate, and allowing the mixture to stand for 24 hours. In order to isolate the product, the alcohol was removed by gentle evaporation, the oily oxime, which, however, rapidly solidifies, collected, washed with water, dried on a porous plate, and purified by recrystallisation from dilute alcohol.

The analysis gave the following numbers:—

0·2110 gram substance gave 11·4 c.c. N; $t = 11°$; bar. = 760 mm.

	Theory. $C_{15}H_{15}NO$.	Found.
N.......	6·22 per cent.	6·43 per cent.

Benzylacetophenoneoxime crystallises from dilute alcohol or light petroleum in colourless needles which melt at 82°. It is readily soluble in alcohol, benzene, chloroform, and hot light petroleum, sparingly in water and cold light petroleum: it is also insoluble in alkalis and dilute acids.

Reduction of Benzylacetophenone: Diphenyl Propyl Alcohol, $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$.

This reduction was carried out by dissolving the pure ketone in ether, floating the solution on water, and cautiously adding about twice the calculated quantity of sodium in small quantities at a time. The ethereal solution was separated, washed with water, dried over calcium chloride, evaporated, and the residual thick oil purified by fractionation under diminished pressure (70 mm.). In this way a fair quantity of a thick, colourless oil was obtained, boiling at about 240° (70 mm.); but there was a considerable residue left in the retort, which probably consists of the corresponding pinacone.

The analysis of diphenyl propyl alcohol gave the following numbers:—

0·1576 gram substance gave 0·1128 gram H_2O and 0·4886 gram CO_2.

	Theory. $C_{15}H_{16}O$.	Found.
C	84 90 per cent.	84·53 per cent.
H	7·55 ,,	7·90 ,,
O	7·55 ,,	7·57 ,,

Diphenyl propyl alcohol is a thick, colourless oil, which, even on long standing, showed no signs of crystallising.

α-Ethyl-β-phenylhydroxypropionic Acid, $C_6H_5{\cdot}CH(OH){\cdot}CH(C_2H_5){\cdot}COOH$.

This acid may be readily prepared from ethyl ethylbenzoylacetate by reduction with sodium amalgam, thus:—

$$C_6H_5{\cdot}CO{\cdot}CH(C_2H_5){\cdot}COOC_2H_5 + H_2 + H_2O = \\ C_6H_5{\cdot}CH(OH){\cdot}CH(C_2H_5){\cdot}COOH + C_2H_5{\cdot}OH.$$

The pure ethereal salt was dissolved in dilute alcohol, and the solution treated in a flat dish with a considerable excess of 2½ per cent. sodium amalgam, in small quantities at a time. The product was separated from the mercury, heated on a water-bath till free from alcohol, acidified with dilute hydrochloric acid, and extracted six times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a thick, almost colourless oil, which, even on long standing, showed no signs of crystallising.

In order to purify this crude product, it was dissolved in an excess of barium hydrate solution, the excess of baryta removed by passing a rapid current of carbon dioxide through the boiling solution, and the filtrate acidified with hydrochloric acid, and extracted six times with ether. The ethereal solution, after being dried over calcium chloride, was evaporated, and the residual colourless oil allowed to stand for some days over sulphuric acid under reduced pressure. The crystalline cake which gradually formed was roughly purified by spreading it on a porous plate, and subsequently recrystallising it from carbon bisulphide.

The analysis gave the following results:—

0·1230 gram substance gave 0·0825 gram H_2O and 0·3074 gram CO_2.

	Theory. $C_6H_5{\cdot}CH(OH){\cdot}CH(C_2H_5){\cdot}COOH$.	Found.
C	68·04 per cent.	68·15 per cent.
H	7·22 „	7·45 „
O	24·74 „	24·40 „

α-Ethyl-β-phenylhydroxypropionic acid melts at 110—112°. It is readily soluble in benzene, alcohol, and boiling water, but only sparingly in light petroleum.

The *silver salt* was prepared by adding silver nitrate to a moderately concentrated neutral solution of the ammonium salt; it is a white, amorphous precipitate sparingly soluble in water. Analysis:—

0·2619 gram substance left on ignition 0·0934 gram Ag.

	Theory. $C_{11}H_{13}AgO_3$.	Found.
Ag......	35·80 per cent.	35·66 per cent.

Action of Heat on α-Methyl-β-phenylhydroxypropionic Acid: Formation of Allylbenzene, $C_6H_5{\cdot}CH{:}CH{\cdot}CH_3$.

When heated at a high temperature, α-methyl-β-phenylhydroxypropionic acid is decomposed with formation of water, carbonic anhydride, and allylbenzene, thus:—

$$C_6H_5{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}COOH = C_6H_5{\cdot}CH{:}CH{\cdot}CH_3 + CO_2 + H_2O.$$

In studying this decomposition, the pure acid* was heated in a small Würtz flask at 280° until the evolution of carbonic anhydride had entirely ceased, the residue rapidly distilled, the colourless distillate dried over potassium carbonate, and submitted to very careful fractional distillation. A considerable quantity of a colourless oil was thus obtained, boiling constantly at 174—175°, but which gave no satisfactory result on analysis.

The whole was therefore redistilled over sodium, the operation being rapidly conducted, in order, as far as possible, to prevent polymerisation, the distillate refractioned, and the oil boiling at 174—175° analysed with the following result:—

0·1238 gram substance gave 0·0947 gram H_2O and 0·4130 gram CO_2.

	Theory. $C_6H_5{\cdot}CH{:}CH{\cdot}CH_3$.	Found.
C......	91·52 per cent.	90·98 per cent.
H......	8·47 „	8·49 „

---

* This acid melts at 95°, and not at 124—125°, as previously stated (Trans., 1886, 49, 160).

Allylbenzene has been obtained by several methods (Beilstein, *Handbuch*, 1888, ii, 126), but the boiling point is variously given as 164 5° and 174—175°. In order, therefore, to be certain of the identity of the substance we had obtained, it was converted into the dibromide by adding to the solution in chloroform the calculated quantity of bromine. On allowing it to evaporate at ordinary temperatures, colourless needles separated, which were dried on a porous plate and analysed with the following result:—

0·2388 gram substance gave 0·3023 gram AgBr.

	Theory. C_6H_5·CHBr·CHBr·CH_3.	Found.
Br.......	53 95 per cent.	53·86 per cent.

This dibromide melts at 66·5°, and agrees in its properties with *αβ*-dibromopropylbenzene (Beilstein, *Handbuch*, 1888, ii, 50).

Condensation of Ethyl Benzoylacetate with Furfuraldehyde. Ethyl Furfuralbenzoylacetate, C_6H_5·CO·C(:CH·C_4H_3O)·$COOC_2H_5$ (?).

This condensation takes place readily when a mixture of ethyl benzoylacetate (10 grams) and furfuraldehyde (5 grams) is heated with excess of acetic anhydride for three hours in a sealed tube at 150°. The resulting brownish-coloured product was freed from acetic anhydride and acetic acid by fractionation, and the residual crude condensation product distilled from a small retort under diminished pressure. The thick, dark-coloured, oily distillate, on standing, gradually solidified to a mass of brownish crystals; these were first roughly purified by contact with a piece of porous plate, and then recrystallised twice from methyl alcohol.

The beautiful, glistening, tabular crystals thus obtained gave on analysis the following numbers:—

0·1598 gram substance gave 0·0760 gram H_2O and 0·4112 gram CO_2.

	Theory. $C_{16}H_{14}O_4$.	Found.
C	71·11 per cent.	71·06 per cent.
H	5·18 „	5·34 „
O	23·71 „	23·60 „

Ethyl furfuralbenzoylacetate melts at 68°. It is readily soluble in alcohol and benzene, but only sparingly in light petroleum.

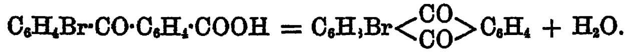
It crystallises from methyl alcohol in remarkably lustrous, four-sided, tabular prisms, which in appearance closely resemble the corresponding benzal compound (Trans., 1885, **47**, 260).

LXXXVIII.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

Note on the Formation of Anthraquinone from Orthobenzoylbenzoic Acid.

By W. H. Perkin, Jun., Ph.D., F.R.S.

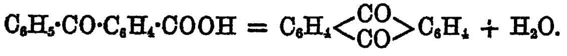
The constitution of anthraquinone and its derivatives has been proved by a number of elegant synthetical experiments, and, among these, the formation of monobromanthraquinone by the dehydrating action of sulphuric acid on orthobromorthobenzoylbenzoic acid (Pechmann, *Ber.*, **12**, 2127) is perhaps the most important—



$$C_6H_4Br{\cdot}CO{\cdot}C_6H_4{\cdot}COOH = C_6H_3Br{<}{\begin{matrix}CO\\CO\end{matrix}}{>}C_6H_4 + H_2O.$$

Liebermann (*Ber.*, **7**, 805) also showed that orthobenzoylbenzoic acid, when heated with fuming sulphuric acid, is converted into anthraquinonesulphonic acid; but no mention has been made of the formation of anthraquinone itself by the action of ordinary sulphuric acid on benzoylbenzoic acid, although it is well known that this change may be brought about by anhydrous phosphoric acid.

In the course of some experiments on benzoylbenzoic acid, I observed that this acid, in contact with ordinary sulphuric acid at 100°, is converted readily, and apparently quantitatively, into anthraquinone,



$$C_6H_5{\cdot}CO{\cdot}C_6H_4{\cdot}COOH = C_6H_4{<}{\begin{matrix}CO\\CO\end{matrix}}{>}C_6H_4 + H_2O.$$

The benzoylbenzoic acid employed in these experiments was prepared by acting on a mixture of phthalic anhydride and benzene with aluminium chloride (Pechmann, *Ber.*, **13**, 1612); it was repeatedly recrystallised from water, and thus obtained in long, thick needles, which, after drying at 115—120°, melted at 127°, and gave the following results on analysis:—

0·1420 gram substance gave 0·0568 gram H_2O and 0·3863 gram CO_2.

	Theory. $C_{14}H_{10}O_3$.	Found.
C	74·34 per cent.	74·19 per cent.
H	4·43 "	4·60 "
O	21·23 "	21·21 "

If this pure acid is dissolved in sulphuric acid, the yellow solution heated at 100° for half an hour, and the product poured into water, a white precipitate separates which consists for the most part of anthraquinone. The crude substance was collected, washed with water, digested with sodium hydrate solution to remove any unchanged acid, dried on a piece of porous plate, recrystallised from glacial acetic acid, and finally sublimed. In this way deep-yellow needles were obtained which melted at 275°, and consisted of pure anthraquinone.

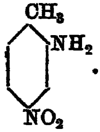
This conversion of benzoylbenzoic acid into anthraquinone by means of sulphuric acid may be carried out well on the small scale as a lecture experiment. A small quantity of the finely divided acid is mixed in a test tube with sulphuric acid, the mixture heated at about 150° for a few seconds, and until the whole of the benzoylbenzoic acid has dissolved; the resulting deep-brown solution is then poured into water. If now an excess of sodium hydrate is added, the anthraquinone remains undissolved. and may be readily identified by warming with a little zinc-dust, when the well-known, characteristic, red-coloured liquid is obtained, which, if decanted and shaken with air, again deposits anthraquinone.

Heriot Watt College, Edinburgh.

LXXXIX.—*The Ortho- and Para-nitro-derivatives of Orthotoluidine.*

By Arthur G. Green and Thos. A. Lawson, Ph.D.

Nölting and Collin (*Ber.*, 17, 265) have shown that by the nitration of orthotoluidine in presence of a large excess of sulphuric acid at a low temperature, the entering NO_2 group assumes the *meta*-position relatively to the NH_2 group, producing paranitro-orthotoluidine,



. This nitrotoluidine appears to be regarded by Nölting and Collin as the sole product of the reaction: this is not the case, however, as although it constitutes at least 75 per cent. of the whole, we have been able to prove the presence of from 3 to 4 per cent. of *meta*nitro-orthotoluidine, $C_6H_3(CH_3)(NH_2)\cdot NO_2$ [1 : 2 : 5], and to isolate a still larger quantity (about 20 per cent.) of the *ortho*nitro-orthotoluidine [$C_6H_3(CH_3)(NH_2)\cdot NO_2$ 1 : 2 : 6]. The latter has, up to the present, only been obtained by the partial reduction of orthodinitrotoluene, $C_6H_3(CH_3)(NO_2)_2$ [1 : 2 : 6] (Cunerth, *Annalen*, **172**, 223; Bernthsen, *Ber.*, **15**, 3018), so that its formation by the direct nitration of orthotoluidine is a matter of some interest. The orthonitro-orthotoluidine presents considerable analogies to the paranitro-orthotoluidine, since the NO_2 group in each stands in the meta-position relatively to the NH_2 group, and from this fact also their simultaneous formation in the nitration of orthotoluidine might have been inferred. Having at our disposal considerable quantities of these two isomers, we considered it would be of interest to make a more complete comparison of these bases and their derivatives than has yet been done.

The orthonitro-orthotoluidine was separated from the paranitro-orthotoluidine by means of its greater solubility in water, and was obtained pure by crystallising its hydrochloride. The orthonitro-orthotoluidine thus obtained crystallises from alcohol in beautiful, bright-yellow, slender needles, whereas the para-compound forms large, orange prisms.

In accord with Bernthsen, we have found the melting point to be 91·5°. It is soluble in about 75 parts of boiling water, the para-compound requiring about 100 parts for solution. Its volatility with steam is about the same as that of the para-compound, namely, 1 part with 1250 parts of water. It boils at about 305° under ordinary atmospheric pressure, but with great decomposition: the para-compound boils a few degrees higher. It differs from the para-compound in being tasteless, the latter having an intensely sweet taste which is not possessed by any of the other nitrotoluidines. Its hydrochloride forms flat needles or plates which are partly basified by water.

The acetyl derivative was obtained in white needles melting at 157—158° uncorr. The benzoyl derivative formed slender, white needles, sparingly soluble in cold alcohol, and melting at 164—165° uncorr. These melting points agree with those found by Ullmann and by Bernthsen.

The identity of our nitrotoluidine with that obtained by Cunerth, Bernthsen, and others from 1:2:6-dinitrotoluene was proved by the complete correspondence of the properties of the base and of its acetyl and benzoyl derivatives, by its giving the *consecutive* tolylenemetadiamine on reduction, and the orthonitro-orthocresol of melting point 143° on boiling the diazo-compound with water. For complete confirmation, the NH_2 group was eliminated by warming the diazo-compound with alcohol: *ortho*nitrotoluene was thus obtained in good yield, and was identified by its boiling point (218° uncorr. at 754 mm.), and by its giving *ortho*nitrobenzoic acid, of sweet taste, and melting point 146°, on oxidation with potassium permanganate.

An attempt to eliminate the NH_2 group by the hydrazine method (reduction of the diazo-compound with stannous chloride and boiling with copper sulphate) gave, instead of orthonitrotoluene, an almost theoretical yield of orthochloro-orthonitrotoluene, $C_6H_3(CH_3)Cl{\cdot}NO_2$ [1 : 2 : 6], identical with that obtained by the action of reduced copper upon the diazochloride (see below).

In correspondence with the fact that these two nitrotoluidines are amido-derivatives of ortho- and para-nitrotoluene respectively, we have found that they behave with alcoholic soda in a manner similar to the nitrotoluenes from which they are derived; for whilst the paranitro-orthotoluidine, when boiled with alcoholic soda, gives (like paranitrotoluene) a deep magenta coloration, the orthonitro-orthotoluidine (like orthonitrotoluene) gives no colour.

Although both nitrotoluidines can be readily brominated in hot acetic acid solution, they offer considerable resistance to other substituting agents: thus, the orthonitro-orthotoluidine is only sulphonated by sulphuric anhydride at the high temperature of 140—150°, whilst the paranitro-orthotoluidine, under the same conditions, is not sulphonated, but undergoes complete decomposition. Moreover, by nitration in sulphuric acid solution, we were unable to introduce a second nitro-group into either isomer.

Alkaline Reduction.

By reducing paranitro-orthotoludine with sodium amalgam, Limpricht and Graeff (*Ber.*, **18**, 1404; *Annalen*, **229**, 340) obtained the corresponding azoxytoluidine, $C_6H_3(CH_3)(NH_2){\cdot}N_2O{\cdot}C_6H_3(NH_2){\cdot}CH_3$, and azotoluidine, $C_6H_3(CH_3)(NH_2){\cdot}N_2{\cdot}C_6H_3(NH_2){\cdot}CH_3$.

In place of sodium amalgam, most other alkaline reducing agents can be used, but we have found sodium stannite to give the best results in the preparation of the azoxy- and azo-derivatives, both from the paranitro- and also from the orthonitro-orthotoluidine. For this purpose, the nitrotoluidine was dissolved in boiling water, and to the boiling solution there was slowly added a cold, aqueous solution of sodium stannite, prepared by mixing solutions of rather more than the calculated quantity of stannous chloride and an equal weight of caustic soda. The azoxytoluidine which separates is purified by crystallisation from toluene. The azotoluidine was obtained by further reduction of the azoxytoluidine, by means of sodium stannite in alcoholic solution: the azoxytoluidine was dissolved in alcohol, and to the boiling solution an aqueous alcoholic solution of the calculated quantity of sodium stannite was added; after boiling for some time, the product was precipitated by the addition of water, and purified by crystallisation from toluene. By the same method of reduction, we have also prepared the azoxytoluidine and azotoluidine corresponding to orthonitro-orthotoluidine; these have not before been obtained. The parahydrazo-orthotoluidine described by Limpricht and Graeff we have been unable to obtain, neither were we able to isolate the orthohydrazo-orthotoluidine, on account of the great rapidity with which it is oxidised to azotoluidine by the air.

Parazoxyorthotoluidine,

$$[1:2:4]\ C_6H_3(CH_3)(NH_2)\cdot N_2O\cdot C_6H_3(NH_2)\cdot CH_3\ [4:2:1],$$

forms yellow needles (from alcohol) or orange prisms (from toluene). The melting point was found to be 168° uncorr., as given by Limpricht and Graeff. The diacetyl derivative, obtained by adding acetic anhydride to a boiling acetic acid solution of the base, forms small, white needles, moderately soluble in hot acetic acid, but only very sparingly in alcohol. It melts at 290° uncorr.

Parazo-orthotoluidine,

$$[1:2:4]\ C_6H_3(CH_3)(NH_2)\cdot N_2\cdot C_6H_3(NH_2)\cdot CH_3\ [4:2:1],$$

forms dark-orange, prismatic needles (from toluene). The melting point was found to be 203° uncorr., whilst Limpricht and Graeff give 197°. The diacetyl derivative, prepared as above, forms small, orange-yellow needles, moderately soluble in boiling acetic acid. It melts at 300° uncorr.

Orthazoxyorthotoluidine,

$$[1:2:6]\ C_6H_3(CH_3)(NH_2)\cdot N_2O\cdot C_6H_3(NH_2)\cdot CH_3\ [6:2:1],$$

crystallises from toluene in straw-yellow plates, easily soluble in toluene, acetic acid, and alcohol, slightly soluble in water. It melts at 149° uncorr. Its hydrochloride forms white plates, sparingly soluble in dilute hydrochloric acid, easily in water. The diacetyl derivative, obtained by adding acetic anhydride to the boiling alcoholic solution of the base, forms small, white, flattened needles, nearly insoluble in alcohol, acetic acid, toluene, &c. It melts at 307°.

Orthazo-orthotoluidine,

$$[1:2:6]\ C_6H_3(CH_3)(NH_2)\cdot N_2\cdot C_6H_3(NH_2)CH_3\ [6:2:1],$$

crystallises from toluene in orange plates, easily soluble in toluene, alcohol, &c. It melts at 175° uncorr. Its hydrochloride forms an orange, crystalline powder, sparingly soluble in water, especially in presence of hydrochloric acid. The diacetyl derivative crystallises from acetic acid in very small, orange-yellow needles. It is very sparingly soluble in boiling acetic acid, insoluble in alcohol, and melts above 340°.

Acid Reduction.

Whilst the paranitro-orthotoluidine is converted by complete reduction (with tin and hydrochloric acid, for example) into the ordinary tolylenediamine, $C_6H_3(CH_3)(NH_2)_2$ [1 : 2 : 4], the orthonitro-orthotoluidine gives rise to the consecutive tolylenediamine,

$$C_6H_3(CH_3)(NH_2)_2\ [1 : 2 : 6]$$

(Ullmann, *Ber.*, **17**, 1959). We have also prepared the latter diamine by reduction of the orthonitro-orthotoluidine formed by nitration of orthotoluidine; the base crystallises in prismatic needles, apparently of the same form as the ordinary tolylenediamine, since the latter causes it to crystallise. We found the melting point to be 105°, whilst Ullmann gives 103·5°. The hydrochloride forms large, flat plates, moderately soluble in water.

Its *diacetyl derivative* melts at 202—203° uncorr., and has the very peculiar and distinctive property of subliming, when heated, in white, excessively light, woolly flocks, immediately over the melted substance, and these, becoming disengaged, float about in the air; these flocks consist of masses of very fine needles. The diacetyl derivatives of other tolylenediamines which we have examined do not show this property in the slightest degree.

Displacement of the NH_2 *Group by Chlorine.*

The displacement of the NH_2 group in the nitrotoluidines by chlorine takes place very readily by employing Gatterman's modification of Sandmeyer's reaction. On adding precipitated copper to a cold solution of the diazochloride containing excess of hydrochloric acid, a vigorous evolution of nitrogen takes place, and, when the reaction is complete, the chloronitrotoluene is obtained in nearly theoretical quantity by distilling the product with steam.

Orthochloroparanitrotoluene, $C_6H_3(CH_3)Cl{\cdot}NO_2$ [1 : 2 : 4], obtained as above from paranitro-orthotoluidine, crystallises from alcohol in long, white, pointed needles, having an odour resembling that of paranitrotoluene. Its melting point was found to be 68°. The same compound has been prepared by Wachendorff (*Annalen*, **185**, 273) and by Lellmann (*Ber.*, **17**, 537) by chlorination of paranitrotoluene with antimony pentachloride, and its melting point is given as 65·5°.

Orthochloro-orthonitrotoluene, $C_6H_3(CH_3)Cl{\cdot}NO_2$ [1 : 2 : 6], obtained as above from orthonitro-orthotoluidine, crystallises from dilute alcohol in white needles of peculiar odour, resembling that of metachloronitrobenzene. It melts at 37° and is readily volatile with steam. As this melting point lies very close to that of the chloronitrotoluene (m. p. 38°) obtained by Beilstein and Kuhlberg (*Annalen*, **158**, 338) from orthoparadinitrotoluene, and to which they assigned the constitution [$CH_3 : Cl : NO_2 = 1 : 4 : 2$], we prepared the latter for comparison by treating the diazochloride of the orthonitroparatoluidine

	CH_3 NH_2 NO_2.	CH_3 OH NO_2.	CH_3 NH_2 NH_2.	CH_3 $NHAc$ $NHAc$.	CH_3 NH_2 N_2O.	CH_3 $NHAc$ N_2O.	CH_3 NH_2 N_2.	CH_3 $NHAc$ N_2.	CH_3 Cl NO_2.	CO_2H Cl NO_2.
1 : 2 : 4	107° (Nölting and Collin), 107·5° (G. and L.). Orange prisms; very sweet.	107—108° (Nölting and Collin). Fine, yellowish needles; very sweet.	99°. Prismatic needles.	221° (Tiemann), 221° (Ladenburg). Does not sublime in flocks.	168° (Limpricht) (G. and L.). Yellow needles or orange prisms.	200° (G. and L.). Small, white needles.	197° (Limpricht), 203° (G. and L.). Orange, prismatic needles.	300° (G. and L.). Small, yellow needles.	65·5° (Wachendorff), 68° (G. and L.). Long, white needles.	136—137° (Wachendorff).
1 : 2 : 6	91·5° (Bernthsen) (G. and L.). Bright-yellow needles; not sweet.	142—143° (Ullmann), 143—144° (G. and L.). Yellow needles; slightly sweet.	103·5° (Ullmann), 105° (G. and L.). Prisms.	202—203° (G. and L.). Sublimes in very light flocks.	149° (G. and L.). Pale-yellow plates.	307° (G. and L.). Small, white, flat needles.	175° (G. and L.). Orange plates.	Above 340° (G. and L.). Small, yellow needles.	37° (G. and L.). Long, white needles.	161° (G. and L.). White, prismatic needles.

(m. p. 78°) with precipitated copper in the same way as the preceding. The chloronitrotoluene thus prepared crystallises from dilute alcohol in white needles, is readily volatile with steam, and melts at 38°, as given by Beilstein and Kuhlberg. In appearance and properties it closely resembles the chloronitrotoluene of melting point 37°, but differs slightly in odour.

In order to prove beyond all question that they are not identical, the two substances were oxidised with potassium permanganate under the same conditions. Beilstein and Kuhlberg's chloronitrotoluene of melting point 38° gave the chloronitrobenzoic acid,

$$C_6H_3(COOH)Cl{\cdot}NO_2\ [1:4:2],$$

prepared by Varnholt (*J. pr. Chem.* [2], **36**, 30). It melted at 140—141° uncorr., whilst Varnholt gives 138—139°. The new chloronitrotoluene of melting point 37° gave a new chloronitrobenzoic acid, $C_6H_3(COOH)Cl{\cdot}NO_2$ [1 : 2 : 6], which was easily soluble in water, and crystallised from it in white, prismatic needles of melting point 161° uncorr.

Our thanks are due to Messrs. Brooke, Simpson, and Spiller (Limited), in whose laboratory at the Atlas Works the above research was conducted.

Summary.

On the preceding page is a tabulated comparison of melting points and chief properties of the two series of compounds.

XC.—*Phosphorous Oxide.* Part II.

By T. E. Thorpe, F.R.S., and A. E. Tutton, Demonstrator of Chemistry at the Royal College of Science, South Kensington.

Action of Light.—In our first communication on this subject (Trans., 1890, 553), we stated that phosphorous oxide was acted upon by light. Even diffused daylight turned it yellow, and in strong sunshine it rapidly became dark-red. On melting the residual oxide and decanting it from the red product, and redistilling it, the clear, colourless substance, on exposure to sunshine, quickly became red as before.

Further observation, however, has rendered it doubtful whether *pure* phosphorous oxide is affected by light. We have been able, as a matter of fact, to prepare a sample of crystallised phosphorous oxide which, after a year's continuous exposure to light, has not suffered the slightest change in colour. A few grams of the freshly-distilled and apparently pure oxide were sealed up in a tube previously filled with dry carbon dioxide. It was then placed in the direct rays of the sun, when it rapidly became red. After nearly three months' exposure to light, the dark-red substance was warmed to the melting point of the oxide, passed through glass-wool to remove the suspended red powder, and the oxide again distilled into a fresh tube, in which it solidified in large, transparent, colourless crystals. On again exposing the crystals to light, they ultimately became as deeply-red as before. The operations of melting, filtering, and distilling were repeated a third time, but the result was the same. Finally, the oxide was simply melted at the lowest possible temperature, filtered through glass-wool, and again exposed to sunshine. It was no longer acted upon by light, but has remained perfectly clear and colourless after nearly 12 months' exposure.

The red substance is the so-called amorphous modification of phosphorus. Although the distilled oxide, when exposed to light, eventually becomes dark-red, the actual extent of decomposition is not very considerable. We have determined the weight of red phosphorus formed in one case after four months, and in another after seven months' exposure. In the first instance it was 0·8 per cent. of the total weight of oxide; in the other case it was 1·0 per cent.

We have made many attempts to obtain preparations of the oxide which should be unaffected by light, by distillation, at the ordinary temperature, in a vacuum; but however many times the same specimen was redistilled in a Sprengel vacuum, it invariably became red on exposure to light. Frequently, however, large, isolated crystals of the oxide of perfect form were obtained by slow spontaneous sublimation in a vacuum, which retained their clear, transparent appearance for days. If, however, the crystals were melted by the warmth of the hand, the liquid drops, on solidification in the wax-like form, rapidly became red. Indeed, it seems not improbable that the permanency of the crystallised oxide is in some way connected with its crystalline character.

It is of course important to determine the bearing of these observations on the question of the phosphorescence of phosphorous oxide. We have repeated our original experiments with samples of oxide which have been several times exposed to light and afterwards distilled in a vacuum, but in no case did the phosphorescence show any diminution in intensity.

Action of Bromine.—Liquid bromine acts violently upon phosphorous oxide, and the mass generally inflames. To study the nature of the change, a known quantity of the recently distilled oxide was placed in a closed glass apparatus so arranged that it could be continuously acted upon at the ordinary temperature by bromine vapour. Small, lemon-yellow, and perfectly homogeneous crystals quickly made their appearance above the oxide. These continued to grow until they were about 2 mm. in diameter; they consisted of short prisms, terminated at both ends by pyramids. It was impossible to determine their crystallographic characters with greater precision, as they deliquesced immediately when in contact with the air. Quantitative analysis showed that they consisted of pure phosphorus pentabromide. The numbers obtained were as follows:—

0·4350 gram of crystals gave 7·57 per cent. phosphorus and 93·32 per cent. bromine.

PBr_5 contains 7·19 per cent. phosphorus and 92·81 per cent. bromine.

The oxide in the flask quickly became covered with a white, amorphous powder, resembling phosphorus pentoxide. After a time both it and the crystals became dissolved in the excess of bromine which condensed upon them. When the reaction was apparently complete, the contents of the flask were distilled. A small quantity of bromine first appeared, after which the thermometer suddenly rose to 190°, and a quantity of phosphoryl bromide passed over and solidified in the receiver. It boiled constantly at 195° (corr.), and melted at 45°. The residue in the flask consisted of a dark, resinous mass, resembling the so-called "metaphosphoryl chloride" of Gustavson (compare G. N. Huntley, this vol., p. 202); it probably consisted of the bromine analogue of that compound. The first action of bromine upon phosphorous oxide appears, therefore, to result in the formation of phosphorus pentabromide and phosphoric oxide.

$$5P_4O_6 + 20Br_2 = 8PBr_5 + 6P_2O_5.$$

The pentabromide crystals are afterwards washed down upon the pentoxide by the excess of bromine, and the two substances then react, forming the oxybromide and "metaphosphoryl bromide." Hence the ultimate action of bromine upon phosphorous oxide appears to be similar to that of the action of chlorine. The reaction may thus be represented:—

$$P_4O_6 + 4Br_2 = 2POBr_3 + 2PO_2Br.$$

The yield of phosphoryl bromide actually obtained was very nearly that required by this equation.

Action of Iodine.—Iodine reacts very slowly with phosphorous oxide, forming an orange-red solid. Even when the substances are heated together in a sealed tube at 150°, the reaction is far from complete.

When the two substances are heated, under pressure, with a quantity of carbon bisulphide, phosphoric oxide is formed, and orange-red prisms of P_2I_4 separate out from the concentrated solution. No formation of the tri-iodide could be detected. The main reaction is probably in accordance with the equation

$$5P_4O_6 + 8I_2 = 4P_2I_4 + 6P_2O_5.$$

Action of Hydrogen Chloride.—This gas is rapidly absorbed by phosphorous oxide with the formation of a viscous mass and a clear, mobile liquid. The semi-solid substance is at first quite white, but as the reaction proceeds it changes to yellow and orange. The clear liquid consists of phosphorus trichloride, boiling at 76°; the semi-solid residue is, for the most part, soluble in water, and the solution contains phosphorous and phosphoric acids. The yellow solid was identified as free phosphorus. With a view of obtaining a quantitative determination of the nature of the change, a weighed quantity of phosphorous oxide, contained in a small distilling flask, was connected with a graduated gas eprouvette standing over mercury, and which could be replenished from time to time with dry hydrogen chloride as the absorption proceeded. By noting the volume of gas absorbed, and checking the amount by occasionally weighing the flask, the amount of the reacting hydrogen chloride could be ascertained. The main action may be represented by the equation

$$P_4O_6 + 6HCl = 2PCl_3 + 2H_3PO_3.$$

Geuther (*J. pr. Chem.* [2], 8, 359) has pointed out that phosphorus trichloride reacts with phosphorous acid to form yellow phosphorus and orthophosphoric acid, and our own observation confirms the statement. The reaction is probably

$$PCl_3 + 4H_3PO_3 = 3H_3PO_4 + P_2 + 3HCl.$$

In an actual experiment carried out by the above method, but in which the reaction was not quite complete even after a week's duration, we obtained from 5 grams of phosphorous oxide a little over 4 grams of phosphorus trichloride, 1·5 grams of orthophosphoric acid, 0·4 gram of phosphorus and 2·7 grams of phosphorous acid.

Action of Sulphur.—When phosphorous oxide and sulphur are heated together in an atmosphere of carbon dioxide or nitrogen, the two substances at first melt and form separate layers of liquid At about 160°, however, a violent reaction occurs, and the mixture becomes solid. No gas is produced. The solid substance is an addition product, having, as we shall show, the formula $P_4O_6S_4$. Direct experiments have proved that it is formed quantitatively in accordance with the equation

$$P_4O_6 + 4S = P_4O_6S_4.$$

It may be obtained in well-formed crystals by sublimation in a vacuum, or by crystallisation from carbon bisulphide. We propose to call it *phosphorus sulphoxide.*

Phosphorus sulphoxide may be readily prepared in the following manner:—From 3 to 5 grams of recently-distilled phosphorous oxide are transferred to the bottom of a strong glass tube, closed at one end, and previously filled with dry carbon dioxide or nitrogen. The requisite amount of sulphur, preferably in the form of small crystals, calculated for the above reaction is then added, and the tube sealed at the blowpipe, and immersed for the lower half of its length in a bath of glycerin, the temperature of which is gradually raised. No reaction is apparent up to 155°, the sulphur merely melting at 115°, and forming a layer below the phosphorous oxide. At a temperature varying in different experiments from 154° to 168°, the lower layer of sulphur is suddenly projected into the phosphorous oxide, and the whole mass is violently thrown up to the top of the tube, with a distinct rushing sound.* In two or three seconds, during which time the contents of the tube are in rapid motion, the reaction is complete, and the internal walls of the tube are seen to be covered in the cooler portion with feathery, colourless crystals, together with compact masses of a yellowish-grey, crystalline solid, which fuses to a viscous liquid in the more strongly heated portion of the tube. The heating may, of course, be carried out in an air-bath, but in that case it is impossible to observe the curious phenomena accompanying the reaction. The product is next transferred to a similar tube, which is then exhausted by the Sprengel pump and sealed. On heating the lower half of the vacuous tube, the sulphoxide sublimes in perfectly colourless, strongly-refractive crystals. The sublimation begins at about 90°, but the most favourable temperature is about 140—150°. A portion of the sublimate at first condenses as a viscous liquid which subsequently solidifies to a colourless, vitreous or crystalline mass; a large proportion, however, always condenses in the form of feathery aggregations, or long needles extending across the tube, or isolated rectangular crystals. Analysis has shown that these various forms of the sublimate possess the same composition.

Phosphorus sulphoxide melts at about 102°, and boils constantly at 295° (corr.). The melting point is not very sharp, as the substance seems to become somewhat viscous before it actually liquefies. The distilled sulphoxide is pale-yellow, and almost wholly sublimes in a vacuum in the form of the colourless crystals above described. Three distinct preparations, analysed by oxidation with bromine-water and determination of the phosphorus by magnesia mixture and the sulphuric acid by barium chloride, yielded the following results:—

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* It is important that the quantities taken should not exceed the amounts specified, for if more than 5 grams of phosphorous oxide and its equivalent of sulphur are employed, the reaction is so violent that it usually results in a loud explosion, the tube being shattered into fragments. The explosion is accompanied by the production of an intensely bright flame.

	I.	II.	III.	Calculated for $P_4O_6S_4$.
Phosphorus ...	35·81	35·71	35·94	35·63
Sulphur	36·08	36·88	36·36	36·78

It was at first surmised that the substance might be a mixed anhydride, that is, phosphoric anhydride in which a portion of the oxygen had been replaced by an equivalent amount of sulphur, or $P_2O_3S_2$; but that it actually has the composition $P_4O_6S_4$, or, in other words, is an additive compound of phosphorous oxide and sulphur, is established by the determinations of its vapour density. These were made by Victor Meyer's method, in an atmosphere of nitrogen, and at a temperature of 350—400°, using a bath of molten lead. No decomposition was evident at this temperature; on cooling, the unaltered substance was found crystallised on the walls of the cylindrical tube. The following results were obtained:—

	I.	II.	III.	Calculated for $P_4O_6S_4$.
Wt. of substance..	0·2853	0·3558	0·2700	—
Density, H = 1...	180·4	171·9	170·8	174
„ air = 1 ...	12·5	11·9	11·8	12·1

Determinations II and III were made with crystals obtained by subliming the distilled sulphoxide in a vacuum.

Phosphorus sulphoxide deliquesces rapidly in air, and hence smells of sulphuretted hydrogen. It is quickly dissolved by water, forming sulphuretted hydrogen and, at first, metaphosphoric acid:

$$P_4O_6S_4 + 6H_2O = 4HPO_3 + 4H_2S.$$

The metaphosphoric acid passes, eventually, rapidly if the solution is evaporated upon a water-bath, into orthophosphoric acid. Phosphorus sulphoxide is readily soluble in twice its volume of carbon bisulphide, from which it crystallises unchanged. It is also soluble in benzene, upon which, however, it reacts, as the liquid becomes dark and sulphuretted products are formed.

The isolated colourless crystals of phosphorus sulphoxide obtained by sublimation in a vacuum consist of rectangular prisms, frequently attaining a length of 2 to 3 mm., and a thickness of from 1 to 2 mm. A large number of crystals have been examined goniometrically and measured, in spite of their rapid deliquescence. This result has been obtained by employing the ingenious little arrangement supplied by

Fuess, of Berlin, with the large horizontal-circle goniometer. The essential part of the arrangement consists of a small closed glass chamber, so shaped as to carry in its lower portion a desiccating substance, such as calcium chloride or phosphoric anhydride, and fitting on the adjusting table instead of the ordinary crystal holder. The crystal is enclosed in this dry chamber during the measurement, and the signal passes from the collimator to the crystal, and from the crystal face to the telescope through two adjacent plate-glass sides.

In the case of every crystal examined, no faces were observed besides those of the rectangular prism and basal plane, all the numerous angles measured being almost and in some cases exactly 90°. On examining the crystals, under the microscope, in parallel polarised light, looking through one of the three pairs of faces, the crystals are always found to be isotropic, while the other faces extinguish parallel to the prism edges. In convergent light, the uniaxial circular rings and dark cross are seen through the isotropic face, provided the crystal is at least 2 mm. thick in this direction; if thinner, only the cross is seen, owing to the feeble double refraction. On rotating the crystal, the cross appears stationary, and does not, unless badly adjusted, break up into hyperbolæ. The crystals, therefore, appear to be uniaxial, or, if biaxial, the angle between the optic axes must be exceedingly small. Hence they are probably tetragonal prisms, terminated by the basal plane.

Although several distinct preparations were made, no other faces were ever observed, the whole of the crystals being homogeneous and exhibiting nothing but pinacoidal faces and basal plane. In order to obtain, if possible, crystals showing further forms, so as to enable the axial ratios to be determined, a considerable quantity of the sulphoxide obtained by sublimation in a vacuum was dissolved in carbon bisulphide, and the latter slowly evaporated in a vacuum from one limb of a V-tube to the other by cooling the second limb with ice. Large, well-formed crystals were again obtained, but they consisted, like those formed by sublimation, of tetragonal prisms terminated by the basal plane and exhibited no other faces whatever.

As previously mentioned, the sulphoxide is sometimes deposited, generally in that part of the tube nearest the surface of the glycerin of the bath, as a colourless, viscous liquid. On cooling, this solidifies to a transparent glass, which sooner or later devitrifies into crystals of the same form as the isolated ones. Generally, the formation of crystals occurs an hour or so after cooling, but in one case devitrification suddenly set in several days after preparation, with production of fantastic feathery aggregations of the rectangular crystals. The fact that the isolated crystals, the vitreous modification, and the feathery and acicular forms are composed of the same substance was proved by direct analysis. The feathery forms are merely aggregations of small, tetragonal prisms, and the needles, similar prisms largely developed in the direction of the vertical axis.

Action of Selenium.—Selenium appears to form a crystalline compound with phosphorous oxide, similar to the sulphoxide, but owing to the fact that the phosphorous oxide is largely decomposed at the temperature of the reaction, the sublimed substance is mixed with the products of the decomposition.

Action of Sulphur Trioxide.—When the vapours of sulphur trioxide and phosphorous oxide are allowed to act on one another in a closed apparatus at the ordinary temperature, white flocks of phosphoric anhydride are deposited upon the walls of the apparatus, and sulphur dioxide is liberated. When the two oxides are separately placed at the two ends of a closed tube fitted with a side tube connected with a gas cylinder standing over mercury, and the phosphorous oxide is slowly melted down upon the sulphur trioxide, a somewhat violent reaction occurs with evolution of heat, formation of phosphoric anhydride, and liberation of sulphur dioxide. Even when the reaction is moderated by cooling with ice, no compound of the two oxides appears to be formed, but merely an oxidation of the phosphorous oxide at the expense of the sulphur trioxide.

Action of Sulphuric Acid.—Concentrated sulphuric acid dropped upon phosphorous oxide occasions a great rise of temperature. Sulphur dioxide is liberated and the phosphorous oxide becomes oxidised to phosphoric acid. When quantities of a gram and upwards are employed, the reaction is so violent that the mass generally ignites.

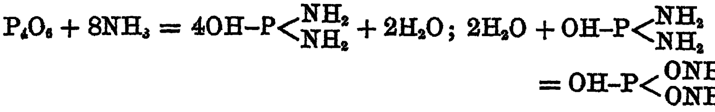
Action of Sulphur Chloride.—Sulphur chloride, S_2Cl_2, acts with great violence on phosphorous oxide, forming phosphoryl and thiophosphoryl chlorides, free sulphur, and sulphur dioxide:

$$P_4O_6 + 6S_2Cl_2 = 2POCl_3 + 2PSCl_3 + 2SO_2 + 8S.$$

Action of Ammonia.—Ammonia slowly reacts in the cold with phosphorous oxide. A small quantity of phosphorous oxide placed in a tube over mercury in an atmosphere of ammonia absorbed a quantity of ammonia corresponding to between 7 and 8 mols. of ammonia per mol. of phosphorous oxide. When ammonia is led over phosphorous oxide melted by the warmth of the hand, in an apparatus previously filled with nitrogen, a somewhat violent reaction occurs with production of a white cloud; the mass ignites, and a considerable quantity of amorphous phosphorus or the red suboxide is formed. The violence of the reaction may, however, be controlled by surrounding the flask with iced water. On removing the cold bath and again melting by the hand, the same sudden combination with production of flame occurs.

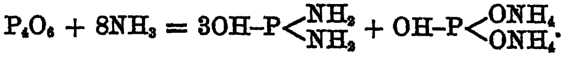
The reaction between ammonia and phosphorous oxide is more easily regulated when the phosphorous oxide is dissolved in benzene or ether. When benzene was used as the solvent, the reaction was accompanied by a rise of temperature to about 50°, necessitating occasional cooling by a cold-water bath. The formation of a white solid begins with the passage of the first bubbles of ammonia, and it is necessary to shake the flask continually so as to prevent the formation of a solid layer upon the surface of the liquid. When no more heating is noticeable upon removing the cold bath, the reaction is at an end, and the benzene may then be evaporated away in a vacuum. If the benzene is distilled off over a water-bath, considerable decomposition occurs. In two experiments performed in an apparatus previously filled with nitrogen, the amount of ammonia taken up corresponded to a little over $6NH_3$ and $7NH_3$ respectively. The reaction is most readily carried out when ether is used as a solvent of the phosphorous oxide, there being but little heating effect even when large quantities are used. 15·63 grams of phosphorous oxide took up 8·46 grams of ammonia, corresponding to a little over $7NH_3$. The same white product is obtained as in the case of phosphorous oxide dissolved in benzene, together with smaller quantities of a yellowish, viscous or deliquesced substance. The ether may readily be removed by gently warming in a current of nitrogen. An analysis of 0·843 gram of the solid white substance, separated as completely from the viscous substance as possible, showed the presence of 37·8 per cent. of phosphorus. This corresponds approximately with the hitherto unknown diamide of phosphorous acid, $OH{\cdot}P{<}\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$, which contains 38·7 per cent. of phosphorus. A complete separation of the diamide from the viscous substance is impossible, owing to the highly inflammable nature of the product of the reaction, which takes fire at once in contact with the air.

It appears probable that phosphorous oxide reacts with 8 mols. of ammonia with the formation of 4 mols. of phosphorous diamide and 2 mols. of water, which may further react with production of a molecule of the corresponding di-ammonium salt. The appearance of deliquescence or formation of small quantities of a viscous substance is probably due to the action of the water produced:



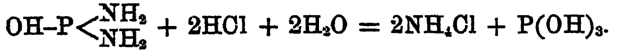
$$P_4O_6 + 8NH_3 = 4OH{-}P{<}\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} + 2H_2O;\ 2H_2O + OH{-}P{<}\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} = OH{-}P{<}\begin{smallmatrix}ONH_4\\ONH_4\end{smallmatrix}.$$

Or



$$P_4O_6 + 8NH_3 = 3OH{-}P{<}\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} + OH{-}P{<}\begin{smallmatrix}ONH_4\\ONH_4\end{smallmatrix}.$$

Phosphorous diamide is a white powder which dissolves instantly in water with sufficient rise of temperature to induce incandescence. When heated in a dry test-tube, ammonia is evolved, then fusion and a partial sublimation occur. Treated with moderately dilute hydrochloric acid, a violent reaction occurs with liberation of non-spontaneously inflammable phosphoretted hydrogen, separation of free phosphorus, and formation of a solution of ammonium chloride and phosphorous and phosphoric acids. The fact that the gas evolved was phosphoretted hydrogen was established by a determination of its vapour density by the method described by Thorpe and Rodger in their paper on "Thiophosphoryl Fluoride" (Trans., 1889, 55, 306). The density obtained was 17·4, that of pure phosphoretted hydrogen being 17·0. In this reaction, the effect of the hydrochloric acid appears to be first to form ammonium chloride and phosphorous acid, but the heat of the reaction is so great that the latter compound is partially converted into phosphoretted hydrogen, phosphoric acid, and free phosphorus:



$$\mathrm{OH{-}P}{<}^{\mathrm{NH_2}}_{\mathrm{NH_2}} + 2\mathrm{HCl} + 2\mathrm{H_2O} = 2\mathrm{NH_4Cl} + \mathrm{P(OH)_3}.$$

Substituted ammonias behave similarly with phosphorous oxide dissolved in ether, forming the corresponding substituted diamides of phosphorous acid, as white and somewhat viscous solids, which evolve phosphoretted hydrogen on the addition of hydrochloric acid, with separation of yellow phosphorus.

Action of Nitrogen Peroxide.—A few grams of phosphorous oxide were placed in one V of a W-tube, and a corresponding quantity of liquid nitrogen peroxide in the other, and the open ends of the apparatus sealed. After some days, it was found that the phosphorous oxide had become converted into a voluminous mass of what was afterwards proved by analysis to be phosphoric anhydride. The red liquid nitrogen peroxide had simultaneously become green. On softening one end of the apparatus in a flame, comparatively little gas escaped. Hence it appears probable that the phosphorous oxide had become oxidised to phosphoric anhydride and the nitrogen peroxide reduced to nitrogen trioxide or nitric oxide, which changed the original colour of the nitrogen peroxide to green. No compound of phosphorous oxide and nitrogen peroxide appeared to be formed, for on dissolving the bulky white substance in water violent hissing occurred, but no red fumes escaped, and the solution gave no reaction with ferrous sulphate.

Action of Phosphorus Pentachloride.—Phosphorus pentachloride reacts somewhat violently with phosphorous oxide, with considerable evolution of heat. The product is a liquid which is raised to its temperature of ebullition, unless the containing vessel is cooled by ice.

The reaction is complete when the proportion of 6 mols. of phosphorus pentachloride to 1 mol. of phosphorous oxide is employed. When the liquid has cooled to the ordinary temperature, and no further rise of temperature occurs on shaking, it may safely be distilled, when it is found to be a mixture of phosphorus trichloride and phosphoryl trichloride:

$$P_4O_6 + 6PCl_5 = 6POCl_3 + 4PCl_3.$$

Action of Phosphorus Trichloride.—Phosphorus trichloride and liquid phosphorous oxide are miscible without action at ordinary temperatures, and practically the whole of the phosphorus trichloride may be distilled off unchanged. When heated together in a sealed tube at 180° for some hours, however, provided the phosphorus trichloride is not present in more than the proportion of 4 mols. to 1 mol of phosphorous oxide, the whole is converted into solid products. As the temperature is rising towards 180°, a white solid commences to be deposited, which rapidly turns yellow and then red. The formation of the solid continues until the whole mixture is solid. The red solid is found to consist of a mixture of phosphorus pentachloride, phosphorus pentoxide, and amorphous phosphorus. The phosphorus pentachloride may be readily extracted by carbon bisulphide. Phosphorus trichloride, therefore, appears to react with phosphorous oxide only at a temperature approaching the boiling point of the latter, and in a closed apparatus under these circumstances does not form phosphoryl trichloride, but a mixture of pentachloride and pentoxide of phosphorus together with amorphous phosphorus.

Hydrogen, phosphoretted hydrogen, carbon monoxide, carbon dioxide, sulphur dioxide, nitrogen, nitric oxide, cyanogen, and ethylene have apparently no action upon either cold or warm phosphorous oxide.

XCI.—*Researches on the Gums of the Arabin Group.* Part II. *Geddic Acids, Gedda Gums; the Dextrorotatory Varieties.*

By C. O'Sullivan, F.R.S.

In Part I of this paper (Trans., 1884, **45**, 41), I described arabic acid and its decomposition products, and gave a general idea of the nature of the lævorotatory gums. Although many new facts connected with some of the decomposition products, especially with arabinose, have since been brought to light, they do not materially alter the general conclusions arrived at and described in the paper indicated. This will be obvious from the facts with which I have to deal in this part, which is devoted to a description of some of the dextrorotatory gums.

Scheibbler (*Ber.*, 6, 612) states that the gum obtained from the beet of one season frequently differs from that from the beet of another in optical activity, that yielded by one season being dextrorotatory and of another lævorotatory. He also shows that gum arabic from different sources does not always rotate the polarised ray in the same direction or with the same power. I have examined many samples of gum arabic—Levantine, Senary, East Indian, and Turkey gum—and although I have found them vary in optical activity, I have not found one sample dextrorotatory. On the contrary, I have found but few samples of gedda gum lævorotatory; the dextrorotatory samples predominated. It is to the latter varieties I shall confine myself on this occasion.

The gum known in commerce as gedda gum is, in appearance, very similar to the inferior kinds of the arabin gums, but, as a rule, the pieces of the former are smaller, and more varied in colour and size than those of the latter. The pieces of the gedda gum are irregular in shape, imperfectly rounded, being evidently rounded masses broken. The general appearance of these gums gives one the idea of a rather heterogeneous mixture.

Sample of Gedda Gum A.

This, the first sample examined, was obtained from the dealers as gedda gum. A few of the whitest and most glassy pieces were selected. This portion was divided into two fractions by dissolving in a little water, partially precipitating with alcohol, in presence of hydrochloric acid, decanting the clear alcoholic solution, and obtaining a further precipitate by adding more strong alcohol. Each fraction was purified by redissolving in water and reprecipitating with alcohol three or four times, and the syrupy precipitates thus obtained were converted into a powder by treating them with alcohol sp. gr. 0·82 and rubbing them down with it. Each portion was then dried, first in a vacuum over sulphuric acid, and finally in a current of dry air at 160° under diminished pressure, and a determination of the optical activity made; that of the more soluble fraction, that is, the one separated from the alcoholic solution by the further addition of strong alcohol, was found to be $[\alpha]_D = +54°$, and that of the less soluble fraction $[\alpha]_D = +45°$. From this it was obvious that even the apparently purest pieces of the gum were not homogeneous, but consisted of a mixture of two or more substances. It was consequently manifest that it was useless to hand-pick the gum, and that the most convenient method of working was to fractionate the material as a whole.

The Ash and Water in the Sample of Gedda Gum A.

Before proceeding with the fractionation of the gum, I thought it desirable to acquire some knowledge of the amount of ash in the gum and the constitution thereof, and also of the amount of water.

The gum was roughly hand-picked into three fractions, viz. :—

A *a*,	consisting of	white pieces.
A *b*,	,,	amber ,,
A *c*,	,,	reddish ,,

15·404 grams of A *a* gave 0·469 gram ash after treatment with ammonium carbonate.

10·534 grams of A *b* gave 0·341 gram ash after treatment with ammonium carbonate.

24·146 grams of A *c* gave 0·738 gram ash after treatment with ammonium carbonate.

An analysis was made of each of these ashes; the results are as follows :—

Percentage on Crude Gum.

	$CaCO_3$.	$MgCO_3$	K_2CO_3.	Total.	Ash calculated from figures given.
A *a*	2·56	0·18	0·27	3·01	3·04
A *b*	2·58	0·38	0·32	3·28	3·24
A *c*	2·30	0·27	3·50	3·07	3·06

A determination of the water was made in each fraction with the following results :—

1·001 grams of A *a*, finely powdered, lost 0·117 gram in a vacuum, and a further 0·031 gram in a current of dry air, at 250 mm. pressure and 100°.

1·515 grams of A *b*, finely powdered, lost 0·204 gram in a vacuum, and a further 0·048 gram in a current of dry air, at 250 mm. pressure and 100°.

1·626 grams of A *c*, finely powdered, lost 0·212 gram in a vacuum, and a further 0·036 gram in a current of dry air at 250 mm. pressure and 100°.

The weight did not become constant in a vacuum over sulphuric acid, but when the loss reached the stage given, the decrease was so slow that I did not consider it of importance, under the circumstances, to continue the drying further; I have no doubt, however, the gum would lose all its water in a vacuum over sulphuric acid at the ordinary temperature.

From these numbers the following percentages are calculated:—

A a = 14·78 per cent. water.
A b = 16·63 „ „
A c = 15·25 „ „

These figures, those obtained for the ash, and its constitution, show, again, that the gum is not homogeneous. I shall have to further consider the ash later on.

The next step was to determine the number and nature of the organic constituents into which the gum could be separated.

The whole gum was dissolved in as little water as possible, the solution placed upon a dialyser and hydrochloric acid added a little at a time until the liquid on the dialyser was found to be free from calcium, and then until the hydrochloric acid had also disappeared, or, at least, until not more than a trace of it remained To the solution thus freed from ash, alcohol of sp. gr. 0·83 was added until about five-sixths of the solid matter therein was precipitated; the precipitate thrown out of solution in this way separated as a syrup, thus differing completely from the arabin gum acids, which, under like conditions, are thrown out as curdy precipitates. When the supernatant liquid became clear, it was decanted off the syrup, and stronger alcohol added to it as long as a precipitate formed; this most soluble portion we shall call fraction *a*. The syrupy precipitate was redissolved in a little water, and alcohol added to the solution in sufficient quantity to throw down three-fourths of the solid matter it contained; fraction *b* was taken out of the clear supernatant liquid by the addition of stronger alcohol. Proceeding in the same way, the second precipitate was divided into fractions *c* and *d*.

A portion of each fraction was converted into a brittle, whitish powder by treatment with alcohol of sp. gr. 0·82. A few grams of each of the powders were dried in a vacuum over sulphuric acid for three or four days and then at 100° under a pressure reduced to 200—250 mm. mercury, until the weight became constant. When these substances are heated at 100° before the greater part of the water and alcohol they contain is eliminated by drying in a vacuum over sulphuric acid, they, like the arabic acids, are so changed as to swell up when afterwards treated with water into a jelly-like mass, without dissolving. They also undergo this change if they are kept in the undried state for a few months. This is the so-called metamodification. On the contrary, when dried as indicated above, they remain soluble and show no sign of being converted into the jelly-yielding modification. A determination of the optical activity of each of the dried fractions was made with the following results:—

a. 4·608 grams substance dissolved to 100 c.c. solution, sp. gr. = 1·01733; optical activity, in a 200-mm. tube, for sodium flame = +5·37°.

b. 8·569 grams substance, 100 c.c. solution, sp. gr. 1·03248; optical activity $\alpha_D = +9{\cdot}29°$, in a 200-mm. tube.

c. 5·090 grams substance, 100 c.c. solution, sp. gr. = 1·01949; optical activity $\alpha_D = +4{\cdot}64°$, in a 200-mm. tube.

d. 8·270 grams substance, 100 c.c. solution, sp. gr. = 1·03237; optical activity $\alpha_D = +5{\cdot}73°$, in a 200-mm. tube.

These numbers lead to the following results:—

a. $[\alpha]_D = +58{\cdot}2°$; D = 3·76.*
b. $[\alpha]_D = +54{\cdot}2°$; D = 3·78.
c. $[\alpha]_D = +45{\cdot}5°$; D = 3·82.
d. $[\alpha]_D = +34{\cdot}6°$; D = 3·91.†

A barium salt of each of these fractions was prepared by exactly neutralising a portion of a solution of each with clear baryta-water, carefully neutralised litmus paper being used as an indicator, adding alcohol, and rubbing down the waxy precipitate with alcohol of sp. gr. 0·82 to a powder. Dried as usual, that is, first in a vacuum over sulphuric acid and finally in a current of dry air at 100° under a pressure of 100—120 mm. mercury, the salts yielded on analyses the following results:—

a = 5·31 per cent. BaO.
b = 5·77 „
c = 6·29 „
d = 7·30 „

The optical activity of the organic portions of the salts was practically the same as that of the free acids before neutralisation.

From these experiments, it is obvious that this sample of gedda gum contains at least two acids of very different optical activity and neutralising power.

It now became necessary to determine if there were more than two acids in the gum. With this object in view, fraction *a* was first examined. To its solution in as little water as possible, sufficient alcohol was added to precipitate a very small quantity of it; this was rejected, and a further addition of alcohol made to the clear supernatant liquid until a quantity estimated at one half the solid matter in solution was thrown out; this fraction, a_2, was allowed to settle until the supernatant liquid became clear, when the remainder of the gum acid was precipitated by adding an excess of strong alcohol; this is called fraction a_1. These gum acids are soluble to a considerable extent in alcohol weaker than sp. gr. 0·87; hence, in dealing with them as indicated here, it is necessary to keep the solutions concentrated. When pure, they are easily "milked," that is, they form, when treated with alcohol, milky solutions in which the further addition of strong alcohol does not produce a precipitate; a drop or two of hydrochloric acid separates the gum acid completely from these solutions. The ammonium, potassium, and sodium salts of these gum acids are not precipitated from their solutions by the careful addition of strong alcohol, but a milky liquid is produced from which most acids precipitate the gum acids. It may, therefore, be that the milking of the gum acid solution with alcohol, as described above, is due to the presence of ammonium salt; I have little doubt, however, that the pure acids can be made to yield milky solutions with alcohol.

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* D = a number calculated from the sp. gr. by rejecting the unit, multiplying the decimal by 1000, and dividing the product by the weight of substance in grams in 100 c.c. solution. It is a good comparative number.

† High D, due to presence of ash.

A determination of the optical activity of fractions a_1 and a_2 yielded the following results:—

$$a_1.\ [\alpha]_D = +58{\cdot}5^\circ.$$
$$a_2.\ [\alpha]_D = +58{\cdot}5^\circ.$$

These numbers are the same as that obtained for the undivided fraction; hence, that portion was a homogeneous substance. In order, however, to have duplicate numbers, I prepared barium and calcium salts of the two fractions a_1 and a_2 for analyses. These salts were made in the same way as the barium salts of the fractions described above. They were dried as usual, and yielded, on analysis, the following results:—

a_1. 1·795 grams barium salt gave 0·1465 grams $BaSO_4$.
1·589 " " 0·1110 " $BaCO_3$.
7·092 " " 100 c.c. solution at 15·5°.

$$\text{sp. gr. } \frac{15{\cdot}5^\circ}{15{\cdot}5^\circ}{*} = 1{\cdot}02932.$$

This solution, in a 200-mm. tube, had an optical activity $\alpha_D = 7{\cdot}73'$.

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* The weight of the liquids at 15·5 compared with the same bulk of water also at 15·5°. These are the conditions under which all the sp. gr. experiments were made.

a_2. 1·996 grams of barium salt gave 0·1625 gram $BaSO_4$.
0·853 „ „ 0·0585 „ $BaCO_3$.
8 158 „ „ 100 c.c. solution at 15·5.
Sp. gr. 1·03386.

This solution, in a 200-mm. tube, had an optical activity $\alpha_D = 9·01°$.

In determining the barium as sulphate in these salts, when the sulphuric acid is added to the solution, the sulphate is precipitated in such a form as does not admit of its being filtered, nor does it settle out; in fact, thrown on to a filter of the very best Swedish paper, it passes through readily. On digesting, however, with an excess of sulphuric acid for some time, until, in fact, the gum acid is broken down, the barium sulphate can be easily separated.

The carbonate was prepared by igniting the salt, and treating the white ash with ammonium carbonate.

The numbers lead to the following results, viz.:—

a_1. 5·36 per cent. BaO from sulphate; 5·42 per cent. from carbonate.
a_2. 5·34 „ „ 5·33 „ „

a_1. $[\alpha]_D = +57·5°$ for organic acid *
a_2. $[\alpha]_D = +58\ 3°$ „
a_1. $D = 4·16$; a_2. $D = 4·15$.

a_1. 1·834 grams calcium salt gave 0·0714 gram $CaCO_3$.
a_2. 1·812 „ „ 0·0641 „

The carbonate was prepared in the same way as the barium carbonate.

7·490 grams calcium salt of a_1 gave 100 c.c. solution at 15·5° of sp. gr. 1·03019. This solution had an optical activity, in a 200-mm. tube, $\alpha_D = +8·60°$.

7·668 grams calcium salt of a_2 gave 100 c.c. solution at 15·5°.of sp. gr. 1·03130. This solution had an optical activity, in a 200-mm. tube, $\alpha_D = 8·84°$.

These numbers lead to the following results:—

a_1. 2·18 per cent. CaO.
a_2. 1·98 „
a_1. $[\alpha]_D = +58·6°$.
a_2. $[\alpha]_D = +58·8°$.
a_1. $D = 4·03$; a_2. $D = 4·08$.

These results leave no doubt that we have a homogeneous substance, in a pure state, to deal with. For reasons which I shall give in the sequel, I propose to call this body *tetrarabinantrigalactangeddic acid.*

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* In all cases the specific rotatory power is calculated for the substance free from ash.

This acid, as I have already to some extent pointed out, differs very materially from arabic acid; it is precipitated from its aqueous solution by alcohol as a syrup, whilst arabic acid is thrown out as a curdy precipitate; it is soluble, to a considerable extent, in alcohol of 0·87, arabic acid is almost insoluble in alcohol of that strength; its optical activity is $[\alpha]_D = +58°$ to $+59°$, that of arabic acid $[\alpha]_D = -24$ to $-25°$; and its barium salt contains 5·33 per cent. of barium, whilst barium arabate yields 6·00 per cent., showing that the geddic acid has a larger molecular weight. With these differences and the many agreements between the two acids, it is a matter of some interest to determine in what relationship they stand one to the other; this shall be a question for future work. I must confine myself, on this occasion, to a consideration of the geddic acid.

We have now to turn our attention to the *b* fraction described above. It was separated, by partial precipitation with alcohol, in the same manner as that described in dealing with fraction *a*, into three fractions, viz., b_1, b_2, and b_3, of which b_1 was the largest and most soluble. A determination of the optical activity of each of these fractions was made after the manner already described when dealing with the *a* fractions, with the following results:—

b_1. $[\alpha]_D = +56·0°$.
b_2. $[\alpha]_D = +49·5°$.
b_3. $[\alpha]_D = +46·8°$.

On again fractionating b_1, a large and most soluble fraction was obtained, the optical activity of which was found to be $[\alpha]_D = +58°$ to $+59°$; a small, least soluble fraction had $[\alpha]_D = +48°$, and there were fractions with intermediate activities; all of these were divisible into a fraction $[\alpha]_D = +58°$, at the most soluble side, and one of $[\alpha]_D = 48°$, at the most insoluble one, there being no indivisible fraction with an activity between the two.

From these figures and facts it is evident that the *b* fraction contained at least two compounds, tetrarabinantrigalactangeddic acid and a substance of lower optical activity.

The whole of the fractions the optical activity of which was $[\alpha]_D = +48°$ to $+49°$, from b_1 and b_2, were mixed, and divided into two, by dissolving in water, adding sufficient alcohol to throw out about one half the solid matter, allowing to stand until the supernatant liquid became clear, decanting, and precipitating the remainder by adding strong alcohol; this, the more soluble portion, we shall call α; the first precipitate is β. The optical activity of these fractions was found to be—

$b\alpha$. $[\alpha]_D = +49\ 0°$.
$b\beta$. $[\alpha]_D = +48·6$.

These, then, constitute a definite and distinct fraction. A barium salt was prepared of the α portion of it, in the way already described.

1·729 grams of this salt, dried as usual, gave 0·160 gram $BaSO_4$.

6·756 grams of this salt, dried as usual, gave 100 c.c. of sp. gr. $=1·02943$. This solution, in a 200-mm. tube, had an optical activity $\alpha_D = +3·14°$.

These numbers lead to the following results:—

$$BaO = 6·08° \text{ per cent.}$$
$$[\alpha]_D = +49·5° \text{ for acid.}$$
$$D = 4·35.$$

Further, the barium salts of several fractions, analyses of which will be given later on, gave percentages of barium oxide varying between 5·9 and 6·1.

It is clear from these factors that we have in this fraction a second acid, in the pure state. For reasons which shall be given, I propose to call it *triarabinantrigalactangeddic acid.*

This acid is equal in neutralising power to arabic acid, but it differs from it in its optical activity; in being, like the former geddic acid, precipitated from its aqueous solutions by alcohol as a syrup; and in being more soluble in alcohol. In fact, there is no difficulty in separating it from arabic acid by fractional precipitation, the arabic acid being thrown out first.

As shown above, the *c* fraction of the gum acid had an optical activity $[\alpha]_D = +45·5°$; in the isolation of the geddic acid just described, many fractions were obtained, all with a lower optical activity than triarabinantrigalactangeddic acid; hence, there must be in the gum a lower rotating acid then that just described.

All those portions with $[\alpha]_D = +43°$ to $+46°$, including the *c* fraction, were mixed, dissolved in a little water, and alcohol gradually added, with continual stirring, until a portion, estimated at 90 per cent. of the total solid matter in solution, was precipitated. The precipitate was allowed to subside, the supernatant liquid, when clear, was decanted off, and strong alcohol added as long as a precipitate was produced. The optical activity of this fraction was found to be $[\alpha]_D = 48—49°$, hence it was triarabinantrigalactangeddic acid. The remaining 90 per cent. precipitated by the first addition of alcohol was again dissolved in a little water, and about 90 per cent. of it precipitated by the gradual addition of alcohol; fraction c_1 was taken from the clear supernatant liquid by adding strong alcohol. The operation was again repeated with the precipitate until fractions c_2, c_3, c_4, and c_5, were obtained, c_1 being, of course, the most soluble. The optical activity of these fractions was found to be

c_1. $[\alpha]_D = +46°$.
c_2. $[\alpha]_D = +43°$.
c_3. $[\alpha]_D = +42°$.
c_4. $[\alpha]_D = +43°$.
c_5. $[\alpha]_D = +36°$.

c_1 admitted of being split up into two fractions, the one $[\alpha]_D = +49°$ triarabinantrigalactangeddic acid on the most soluble side, and the other $[\alpha]_D = +43°$ on the least soluble one, there being no intermediate indivisible fraction.

All the portions $[\alpha]_D = +42°$ to $+43°$, were again mixed and divided into three fractions, $c\alpha$, $c\beta$, and $c\gamma$, $c\alpha$ being the most soluble. An examination of the barium salts of each of these fractions led to the following results:—

2·864 grams salt of $c\alpha$, dried as usual, gave 100 c.c. solution, sp. gr. 1·01222. This solution, in a 200-mm. tube, rotated the polarised ray $\alpha_D = +2·30°$.

2·908 grams salt of $c\beta$, dried as usual, gave 100 c.c. solution, sp. gr. 1·01237. This solution, in a 200-mm. tube, rotated the polarised ray $\alpha_D = +2·33°$.

3·126 grams salt of $c\gamma$, dried as usual, gave 100 c.c. solution, sp. gr. 1·01300. This solution, in a 200-mm. tube, rotated the polarised ray $\alpha_D = 2·50°$.

0·716 gram salt of $c\alpha$, dried, gave 0·072 gram $BaSO_4$.

From these numbers we have the following:—

$c\alpha$. $[\alpha]_D = +43·0°$; D = 4·27; BaO = 6·60 per cent.
$c\beta$. $[\alpha]_D = +42·8°$; D = 4·25.
$c\gamma$. $[\alpha]_D = +42·6°$; D = 4·16.

The D of the salts of the $c\gamma$ fraction shows that the preparation was not quite dry.

Several other barium salts were found to contain from 6·55 to 6·65 per cent. BaO.

This portion which admitted of being thus divided is, therefore, a third acid in a pure state; I shall call it *diarabinantrigalactangeddic acid*. The precipitate of this acid thrown out of the aqueous solution by alcohol is less syrupy than that of the other gum acids described.

Proceeding in the same way with the portions having an optical activity less than $[\alpha]_D = +43°$, I succeeded in eliminating a fraction $[\alpha]_D = +36°$, which admitted of being divided into three fractions of the same optical activity. In doing this there was a less soluble small portion on one side, and the more soluble diarabinantrigalactangeddic acid on the other. This is a fourth gum acid; we shall call it *monarabinantrigalactangeddic acid.* Its calcium salt yielded, on analysis, the following results:—

0·672 gram dried substance gave 0·0428 gram $CaCO_3$.
2·688 grams „ „ 100 c.c. solution, sp. gr. 1·01124.
This solution, in a 200-mm. tube, rotated the polarised ray $\alpha_D = +1·91°$. From these figures we have:—

$$CaO = 3·5 \text{ per cent.}$$
$$[\alpha]_D = +36·7° \text{ for acid.}$$
$$3·50\ CaO = 7·30\ BaO.$$

The portion of the dialysed gum less soluble than this acid, I neglected, as it was small in quantity, much coloured, and not easily worked. I, however, determined that it contained a nitrogenous compound, easily soluble in acids and alkalis, which in alkaline solution gave a beautiful purple colour, when treated with a few drops of alkaline copper solution (Fehling's solution). On boiling this, a portion of the copper oxide was reduced to red oxide; this is due, probably, rather to the presence of some gum acid than to the nitrogenous substance.

I have so far shown that the gum consists of the calcium, magnesium, and potassium salts of four acids, which I have named and characterised as follows:—

Tetrarabinantrigalactangeddic acid, $[\alpha]_D = +58—59°$; per cent. BaO in barium salt = 5·33,
Triarabinantrigalactangeddic acid, $[\alpha]_D = +48—49°$; per cent. of BaO in barium salt = 6·00,
Diarabinantrigalactangeddic acid, $[\alpha]_D = +42—43°$; per cent. BaO in barium salt = 6·60,
Monarabinantrigalactangeddic acid, $[\alpha]_D = +36—37°$; per cent. BaO in barium salt = 7·30,

and a nitrogenous substance of the character of a proteïd.

The names applied to the acids give some idea of their constitution, but, of course, at this stage of the investigation, I did not possess the data which enabled me to apply these terms to them; that knowledge was the result of an examination of the products of the action of sulphuric acid on the acids themselves.

A solution containing 30 grams of tetrarabinantrigalactangeddic acid in 90 c.c. was heated to 92—95° in a water-bath, and 10 c.c. dilute sulphuric acid containing 2 grams acid, heated to the same temperature, was added to it. The digestion was then continued for 15 minutes, when the solution was rapidly cooled. To the cold solution, alcohol of sp. gr. 0·82—0·83° was added as long as a precipitate formed. The sugar or sugars remained in the alcoholic solution, whilst the gum acid or acids were in the precipitate.

I shall deal with the alcoholic solution first. This was neutralised with strong baryta-water, the barium sulphate and a little barium salt of a gum acid allowed to settle, and the clear solution decanted. The precipitate was washed several times on a filter with alcohol of 0·83. and the washings added to the original solution, in which they invariably produced a cloudiness, due to the presence of a little barium salt. The alcoholic liquid was then evaporated, in a vacuum, to a syrup, which, on standing for a few hours, became a mass of crystals; after standing for some days, these were washed with dry methyl alcohol and dried. An examination of the crystals showed that they had a higher optical activity than β-arabinose* (Trans., 1884, **45**, 41), namely, $[\alpha]_D = +115°$; the reducing power being $K = 105—106°$. They were redissolved in a little water and the solution allowed to stand for some time, when crystals appeared, which showed a habit somewhat different from the arabinose from arabic acid, although they undoubtedly belonged to the same system. The sugar agreed in all its other properties with arabinose, its optical activity, &c., being identical, as shown by the following experiments:—

	c.†	D.	$[\alpha]_D$.	K.
I.	4·960	3·828	+104·2°	*a* 108·3. *b* 109·3.
II.	4·459	3·860	+105·4°	110·3.
III.	4·543	3·860	+104·6°	110·3.
IV.	4·846	3·861	+104·7°	109·9.

The mother liquors, those in the methyl alcohol washings as well as the aqueous ones, were mixed and evaporated in a vacuum to a strong syrup. This was treated with dry methyl alcohol, which separated a few grams of barium salt of gum acid; this we shall deal with later. The solution was again concentrated to a syrup in a vacuum, and the syrup dissolved in a little methyl alcohol; this solution yielded a further crop of arabinose on standing. On freeing the mother liquor from alcohol, the optical activity of the solid matter in solution determined from the sp. gr. was found to be $[\alpha]_D = +160°$. Arabinon was isolated from this as described (Trans., 1890, **57**, 59). There was no evidence of any other product; all the factors of the solid matter agreeing with mixtures of arabinon and arabinose.

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* Since the publication of the paper quoted here, much has been done to enable us to identify arabinose absolutely. Had I had the same means at my disposal then, I should not have used the term β-arabinose: the sugar is undoubtedly arabinose, α-arabinose being the sugar I have since described as arabinon.

† *c* = grams per 100 c.c.

There was present, indeed, a small quantity of a non-crystallisable substance of low rotating power, which yielded no mucic acid on treatment with nitric acid, showing the absence of galactose (γ-arabinose) or a galactose-yielding substance. In the paper just quoted, I showed that arabinose, when digested with sulphuric acid for a short time, yields a low-rotating, syrupy substance of the same kind; hence, it can fairly be concluded that the small quantity of the substance mentioned is derived from arabinose by the action of the sulphuric acid. It is, therefore, clearly established that arabinon, arabinose, and the precipitate with alcohol are the only products of the first quarter of an hour's action of sulphuric acid on the geddic acid.

We have now to turn to an examination of the precipitate. This was dissolved in a little water and again precipitated, the operation being repeated until the precipitate was free from sulphuric acid. The alcoholic solutions thus obtained were added to that the results of the examination of which are given above.

A portion of the syrupy precipitate was dissolved in water, and the solution boiled until free from alcohol. The sp. gr. of this solution was found to be 1·03362, hence 8·8466 grams substance in 100 c.c. (taking mean value for sp. gr.), and its optical activity in 200-mm. tube $\alpha_D = +4·45°$. This gives a specific rotatory power for the solid matter $[\alpha]_D = +25°$.

The remainder of the syrup was dissolved in a little water and divided into two fractions, S_2, more soluble, and S_1, less soluble, by treatment with alcohol, as already described. Barium salts were made of a portion of each of these fractions in the usual way. On analysis they yielded the following results:—

0·670 gram S_1, dried at 100°, gave 0·080 gram $BaSO_4$.
0·713 " S_2 " " 0·085 "
2·682 grams S_1 " " 100 c.c. solution, sp. gr. 1 01201, and rotated the ray α_D in 200-mm. tube = +1·21°.
2·852 grams S_2, dried at 100°, gave 100 c.c. solution, sp. gr. 1·01254, and rotated the ray α_D in 200-mm. tube = +1·38°.

From these numbers we have—

S_1. 7·84 per cent. BaO in barium salt.
S_2. 7·83 " " "

S_1. $[\alpha]_D = +24·7°$ for organic acid; $D = 4·48$.
S_2. $[\alpha]_D = +26·3°$ " $D = 4·40$.

A consideration of these factors makes it clear that we had in the precipitate a pure, homogeneous compound; I shall call it *geddinosic* *acid;* it differs completely, as we have seen, from either of the natural gum acids in optical activity and neutralising power.

The gum acid salt of barium precipitated on neutralising the alcoholic solution with baryta-water, and the small quantity of barium salt insoluble in dry methyl alcohol obtained when treating the syrup as described above were, upon examination, found to contain slightly more barium, and to have a somewhat less optical activity than the barium salts just described; the meaning of this will be clear later on.

It was difficult to separate the organic barium salt precipitated with the barium sulphate from the latter; the separation was accomplished, however, by boiling the precipitate with water, filtering, washing the residue with boiling water (the filtrate was quite milky from barium sulphate), evaporating the filtrate till it became moderately concentrated, and then adding alcohol drop by drop until a slight portion of the barium salt was rendered insoluble; this took down with it the barium sulphate, and left the supernatant liquid clear. The organic barium salt was obtained by further addition of alcohol to the clear supernatant liquid.

Geddinosic acid, prepared and purified as above described, was acted upon with sulphuric acid. A solution of it was prepared containing in 100 c.c. about 25 grams of the dry acid, heated in a water-bath, and 2·5 grams of sulphuric acid, previously diluted, added to it. The digestion was then continued for 15 minutes, after which the liquid was allowed to cool, when strong alcohol was added to it as long as a precipitate formed.

The alcoholic solution and the precipitate were examined in the same way as is described above. The solution contained arabinon in very small quantity, arabinose, and a little gum acid. There was no galactose, no mucic acid being produced by the action of nitric acid on the sugars, and other sugars than arabinon and arabinose were proved to be absent by crystallising the arabinose, and finding that the solid matter in the mother liquors, when freed from arabinon, had an optical activity not far removed from arabinose. In this case, however, it must be stated that altogether but very little sugar, in proportion to the geddinosic acid taken, was produced.

The precipitate, purified from sugars and sulphuric acid by repeated precipitation with alcohol, and finally by dialysis, was divided into four fractions by partial precipitation with alcohol, after the manner already described, G_1 being the most, and G_4 the least soluble fraction. The optical activity of these fractions was found to be—

G_1. $[\alpha]_D = +26{\cdot}8^\circ$.
G_2. $[\alpha]_D = +24{\cdot}4^\circ$.
G_3. $[\alpha]_D = +22{\cdot}2^\circ$.
G_4. $[\alpha]_D = +22{\cdot}2^\circ$.

Fractions G_1 and G_2 are practically unaltered geddinosic acid. G_3 and G_4 are products of the action; these were mixed and again divided into two fractions, G α and G β. Barium salts were prepared of portions of each of these fractions; they yielded on analysis the following results :—

1·828 grams of G α, dried as described, gave 0 201 gram $BaCO_3$.
1·803 „ G β „ „ 0·199 „
7·596 „ . G α „ „ 100 c.c. solution, sp. gr. 1·03432, and had an optical activity $\alpha_D = +3{\cdot}08°$ in a 200-mm. tube.
7·434 grams of G β, dried as described, gave 100 c.c. solution, sp. gr. 1·03351, and had an optical activity $\alpha_D = +3{\cdot}02°$ in a 200-mm. tube.

From these numbers we have :—

G α. 8·54 per cent. BaO in the barium salt.
G β. 8·56 „ „ „
G α. $[\alpha]_D = +22{\cdot}2°$ for acid; $D = 4{\cdot}52$ for barium salt.
G β. $[\alpha]_D = +21{\cdot}9°$ „ $D = 4{\cdot}51$ „

These numbers show that this is another acid in the pure state; I propose to call it *trigalactangeddic acid.*

Taking into consideration the very small proportion of sugar produced by this further 15 minutes' action of sulphuric acid on geddinosic acid, this new acid may be looked upon as a distinct resting stage in the action of sulphuric acid on tetrarabinantrigalactangeddic acid. That such is the case was proved by acting on that acid, in the way described, for 40 minutes, when it was found that trigalactangeddic acid, with practically the same neutralising power and optical activity as given above, was the only substance formed in quantity besides the sugars.

As can be seen from these experiments, neither of the acids found ready formed in the gum are amongst the products of even 15 minutes' action of sulphuric acid on the higher acid; hence it would appear that neither of the lower gum acids is a resting stage in the action of sulphuric acid on the higher one. It seemed to me, however, worth determining whether or not it was possible to so modify the action of the sulphuric acid on the higher acid as to obtain one or all three of the lower ones.

50 grams of dry tetrarabinantrigalactangeddic acid, 2·5 grams of sulphuric acid, and 60 grams of water were digested for five minutes at 98—99°. The gum acid was dissolved in a portion of the water, and heated to the temperature mentioned; the sulphuric acid was added

to the remainder of the water, and the diluted acid boiled, the liquids were then mixed, and the digestion continued in a water-bath. At the end of five minutes, the solution was cooled as quickly as possible, and strong alcohol added as long as a precipitate was produced. The alcoholic solution and the precipitate were examined in the same way as has been described in treating of the other conversions.

The sugars in the solutions were arabinon in large quantity, as might be expected, and arabinose; there was no galactose.

In purifying the gum acids from the sugars, the lôw solubility of arabinon in strong alcohol had to be taken into account; the precipitate was dissolved in a little water and alcohol of sp. gr. 0·85 added in insufficient quantity, so as not to precipitate the acids completely. The clear supernatant liquid was then neutralised with baryta-water, upon which a precipitate of barium sulphate and the barium salt of a gum acid were precipitated; these were collected and washed with dilute alcohol. The filtrate was evaporated in a vacuum to a syrup, which was dissolved in a little methyl alcohol, and strong alcohol (0·820) added; some barium salt of a gum acid was precipitated, and the mixture put aside to allow the supernatant liquid to become clear. On examining it at the end of a few days, it was observed that the slight syrupy precipitate and the sides of the vessel were covered with sphero-crystals; these, I have reason to believe, are arabinon. I mention this matter here simply to indicate the direction in which that sugar is to be looked for in quantity, and the possibility of obtaining it in the crystallised state.

The precipitate, with insufficient alcohol, was purified on the lines indicated, and divided into three fractions, T_1, T_2, and T_3, T_1 being the most soluble. The α_D and D of these fractions were determined with the following results:—

3·198 grams T_1, dried as usual, gave 100 c.c. solution, sp. gr. 1·01230; this, in a 200-mm. tube, had an optical activity $\alpha_D = +2·17°$.

3·200 grams T_2, dried as usual, gave 100 c.c. solution, sp. gr. 1·01210; this, in a 200-mm. tube, had an optical activity $\alpha_D = +2·00°$.

2·842 grams T_3, dried as usual, gave 100 c.c. solution, sp. gr. 1·01086; this, in a 200-mm. tube, had an optical activity $\alpha_D = +1·84°$.

From these numbers we have:—

T_1. $[\alpha]_D = +33·9°$; D = 3·85.
T_2. $[\alpha]_D = +31·2°$; D = 3·79.
T_3. $[\alpha]_D = +32·4°$; D = 3·82.

A portion of the purified undivided precipitate was converted into a barium salt.

3·470 grams dry salt gave 100 c.c. solution, sp. gr. 1·01526 ; this, in a 200-mm. tube, had an optical activity $\alpha_D = +1·97°$.
0·867 gram dry salt gave 0·094 gram $BaSO_4$.
Hence $[\alpha]_D = +30·5°$; D= 4·40; BaO = 7·12 per cent.

These correspond sufficiently well with the factors obtained for monarabinantrigalactangeddic acid, and as the barium salt which separated on neutralizing the alcoholic solution, yielded numbers agreeing pretty well with these, it is clear that no higher acid than the monarabinan one was produced in any quantity by the five minutes' action of sulphuric acid on the high gum acid. I am, however, of opinion that by carefully regulating the strength of the solution, the quantity of sulphuric acid, and the temperature, the three lower natural acids of the series can be prepared from the higher one. From this it would, of course, naturally follow that the products of the final action of sulphuric acid on all four acids are the same. This I have proved to be the case.

A solution containing in 90 c.c. 25 grams of triarabinantrigalactangeddic acid was heated to 96—97° in a water-bath, 10 c.c. dilute sulphuric acid containing 2 grams H_2SO_4 added, and the digestion continued for 20 minutes. The cooled liquid was treated with alcohol as described above so as to separate the sugars from the gum acids. On distilling off the alcohol from the final alcoholic solution freed from sulphuric acid, and concentrating to a syrup, a large crop of crystals was obtained; this was higher in optical activity than arabinose; a second crop was obtained which approached very closely to arabinose in optical activity, and a third crop was allowed to form; this agreed with arabinose still more closely. The three crops were washed with methyl alcohol, and recrystallised from water; the crystals were exactly the same in habit as those obtained from tetrarabinantrigalactangeddic acid, and the optical activity of the sugar was found to be—

$$[\alpha]_D = +104·5° \quad c = 3·169,$$

which is the activity of pure arabinose. The methyl alcohol washings and the mother liquors were mixed, and the mixture freed from alcohol by distillation. A determination of the optical activity of the solid matter in solution, which was little in proportion to the arabinose crystallised, gave—

$$[\alpha]_D = +140°,$$

showing the presence of arabinon. There was no galactose present, no mucic acid being produced by the action of nitric acid. I may, however, say that this test for galactose is unnecessary, for if it should be present, the first crop of crystals is always contaminated with it, as is indicated by the crop possessing a lower rotatory power than arabinose.

The gum acids were purified from the sugars as much as possible and divided into two fractions, (1) more, and (2) less, soluble. Barium salts of these were prepared; they yielded on analysis the following results:—

(1) = 7·55 per cent. BaO, and
(2) = 8·03 " "

(1) $[\alpha]_D = +27{\cdot}3°$ for organic acid,
(2) $[\alpha]_D = +23{\cdot}8°$ "

A comparison of these numbers with those obtained for geddinosic acid and trigalactangeddic acid shows very clearly that we have in this product a mixture of both acids; it was not necessary to fractionate it further.

Diarabinantrigalactangeddic acid was acted upon in the same way with the following results:—

The sugars were found to be arabinon and arabinose; there was no galactose.

The purified gum acids were divided into three fractions, D_1, D_2, and D_3, of which D_1 was the most soluble, and of these, barium salts were prepared; they yielded on analyses:—

	Per cent. BaO.	$[\alpha]_D$ for acid free from BaO.
D_1..........	7·56	+26·3°
D_2..........	7·85	+25·8
D_3..........	7·90	+18·8

These numbers also show that we have in the transformed product geddinosic and trigalactangeddic acid. Both the percentage of barium and the optical activity of the D_3 fraction are low, but when we consider that this fraction contained all the impurity of the original acid, we may feel satisfied that the indication is sufficiently distinct to obviate the necessity of further fractionation.

Monarabinantrigalactangeddic acid treated in the same way yielded similar results. The sugars were the same, arabinon, however, being present only in minute quantities.

An analysis of the barium salts of the two fractions into which the gum acids were divided gave the following results:—

	Per cent. BaO.	$[\alpha]_D$ for acid free from BaO.
M_1..........	7·92	+25·1°
M_2..........	8·30	+21·8

There was a small, less soluble fraction than M_2, but as its appearance left no doubt that it contained much impurity, it was neglected. Here, again, we have geddinosic and trigalactangeddic acids, the same products as in the three preceding cases; it is clear, therefore, that all four gum acids break down in the same way, and yield, as a distinct resting stage, the same compound, namely, *trigalactangeddic acid.*

In further support of the conclusion that the resting stage in the action of sulphuric acid on the four acids is the same, I determined the amount of mucic acid yielded by the action of nitric acid on the products from the four sources which agreed in optical activity and neutralising power with trigalactangeddic acid. To 1 part of each of these products, 7·5 parts of nitric acid and 2 5 parts of water were added; the mixture was heated in a beaker of 60 c.c. capacity, covered with a watch glass until red fumes began to be evolved, when the vessel was removed from the source of heat until the violence of the reaction had ceased. Heat was again applied until nitrous fumes were no longer evolved in quantity. On cooling, the contents of the beaker became solid, and after standing a few days the mucic acid was collected on a tared filter, washed with cold water, dried at 100°, and weighed. To the weight thus obtained, *minus* the weight of the filter, a quantity was added proportionate to the bulk of the filtrate; this gave the mucic acid. It was found to vary from 50 to 54 per cent. of the gum acid product employed, but no satisfactorily concordant results were obtained with the acids from either of the four sources, although they all agreed in their variations; in fact, all four products behaved as if they were one and the same substance, and yielded a quantity of mucic acid, not far removed, above or below, from 52 per cent. Although these experiments would not in themselves be conclusive as to the identity of the four products, they materially add to the evidence already adduced, that trigalactangeddic is a distinct resting stage in the action of sulphuric acid on the four natural gum acids of the sample of gedda gum under examination.

I must not omit to point out that acids other than trigalactangeddic acid and geddinosic acids are at times found amongst the products of the transformation; they possess a higher rotatory power and neutralising power than either of these acids. When they appear amongst the products, galactose is found with the sugars. This will be accounted for later on.

Before we proceed any further with this investigation, it would probably be as well to enquire into the meaning of the facts we have established.

To begin with, we have tetrarabinantrigalactangeddic acid, with optical activity $[\alpha]_D = +58°$, the barium salt of which contains 5·33 per cent. BaO, and we find that this is converted in a short time by the action of sulphuric acid into geddinosic acid, $[\alpha]_D = +25°$, the barium salt of which yields 7·8 per cent. BaO, and finally into trigalactangeddic acid, $[\alpha]_D = +22°$, the barium salt of which gives 8·5 per cent. BaO, whilst, at the same time, a large quantity of arabinon and arabinose is formed. With the elimination of the sugars, we see that an acid is produced of a much lower molecular weight than the acid acted upon. If we calculate the molecular weight of each from the percentage of BaO in the barium salt, we have for trigalactangeddic acid $\frac{153 \times 100}{8\cdot5} - 153 = 1647$, and for tetrarabinantrigalactangeddic acid $\frac{153 \times 100}{5\cdot33} - 153 = 2717$; and if we subtract the former from the latter number, 2717 − 1647 = 1070, we get a figure which represents the molecular weight of the material from which the arabinon and arabinose were derived. Does this indicate the multiple of the unknown group *arabinan*, $C_{10}H_{16}O_8$, or of arabinon, $C_{10}H_{18}O_9$? The molecular weight of the former is 264 and of the latter 282; then

$$\frac{1070}{264} = 4\cdot05 \text{ and } \frac{1070}{282} = 3\cdot79;$$

hence, it is more likely that it is four groups of $C_{10}H_{16}O_8$ which are hydrolysed than 3·79 groups of $C_{10}H_{18}O_9$. If, therefore, we take Tg as a formula for trigalactangeddic acid, that of tetrarabinantrigalactangeddic acid will be $4C_{10}H_{16}O_8,Tg$; hence the term *tetrarabinan*. Had it been $4C_{10}H_{18}O_9$ that were removed, the formula of the higher acid would be $4C_{10}H_{18}O_9,Tg$, and its barium salt $4C_{10}H_{18}O_9,Tg,BaO$; this requires 5·22 per cent. BaO, whilst $4C_{10}H_{16}O_8,Tg,BaO$ requires 5·35 per cent. The mean result of many analyses of the carefully-prepared barium salt is 5·33 per cent. BaO, as given above, the variations being only in the second place of decimals; hence, the tetrarabinan formula is well established. I have not been able to determine whether BaO displaces H_2O in these salts or not; I believe, however, the salts are addition products; they certainly are not of the nature of true salts, as I shall be able to show later on.

Let us now see what relation the other acids hold to tetrarabinantrigalactangeddic acid. We found that the barium salt of that acid contained about 6 per cent. BaO, as the mean of the results of many concordant analyses of several different preparations, $3C_{10}H_{16}O_8,Tg,BaO$, that is, tetrarabinantrigalactangeddic acid, *minus* the arabinan group $C_{10}H_{16}O_8$, requires 5·90 per cent. BaO; hence, the second natural gum acid is *tri*arabinantrigalactangeddic acid.

The barium salt of the third acid yielded 6·6 per cent. BaO; $2C_{10}H_{16}O_8,Tg,BaO$, that is, the high acid, *minus* two $C_{10}H_{16}O_8$ groups, requires 6·57 per cent. BaO; hence, this acid is *di*arabinantrigalactangeddic acid.

The barium salt of the fourth acid yielded 7·3 per cent. of BaO; $C_{10}H_{16}O_8Tg,BaO$, that is, the high acid, *minus* three $C_{10}H_{16}O_8$ groups, require 7·41 per cent. BaO; hence, this is *mon*arabinantrigalactangeddic acid.

I showed above that an acid, which I called geddinosic acid, a marked resting stage in the action of sulphuric acid on the gum acids, yields a barium salt which was found to contain 7·84 per cent. BaO. This seems to indicate an acid intermediate between monarabinantrigalactangeddic acid and trigalactangeddic acid; $C_5H_8O_4Tg,BaO$, requires 7·92 per cent. BaO. It is not easy to understand how such a substance can exist and be a product of the action of sulphuric acid on the geddic acid, for it necessitates the representation of the breaking down not by the equations

$$4C_{10}H_{16}O_8Tg + 4H_2O = \underset{\text{Trigalactangeddic acid.}}{Tg} + \underset{\text{Arabinon.}}{4C_{10}H_{18}O_9}$$

and

$$4C_{10}H_{18}O_9 + 4H_2O = \underset{\text{Arabinose.}}{8C_5H_{10}O_5},$$

but by the equations

$$4C_{10}H_{16}O_8,Tg, + 4H_2O = \underset{\text{Geddinosic acid.}}{C_5H_8O_4Tg} + \underset{\text{Arabinon.}}{3C_{10}H_{18}O_9} + \underset{\text{Arabinose.}}{C_5H_{10}O_5}$$

and

$$3C_{10}H_{18}O_9 + 3H_2O = 6C_5H_{10}O_5.$$

There can, however, be no question as to the existence of the acid, for I have taken much trouble to purify it and determine its composition. I record the fact as I found it, and leave to future investigation the task of explaining the matter.

This is a convenient stage to summarise the results hitherto obtained. We have found that the four natural gum acids may be named and represented as follows :—

Tetrarabinantrigalactangeddic acid	$4C_{10}H_{16}O_8,Tg$.
Triarabinantrigalactangeddic acid	$3C_{10}H_{16}O_8,Tg$.
Diarabinantrigalactangeddic acid	$2C_{10}H_{16}O_8,Tg$.
Monarabinantrigalactangeddic acid	$C_{10}H_{16}O_8,Tg$.

Each of these, when acted upon by sulphuric acid, yields as a definite resting point

Geddinosic acid........................ $C_5H_8O_4,Tg$,

and finally

Trigalactangeddic acid .... Tg.

The next step in the investigation was to inquire into the constitution of the last-named acid.

We have seen that this acid is but slightly acted on when digested 25—30 minutes in a solution containing 2—3 per cent. sulphuric acid. On being oxidised with nitric acid, it yielded about 52 per cent. of mucic acid; galactose, oxidised under similar conditions, yielded 85 per cent. of the same acid; it is fair, therefore, to conclude that trigalactangeddic acid contains, at least, 85 : 100 :: 52 : 61 per cent. of a galactose-yielding constituent. Such being the case, it was to be expected that the acid would yield galactose when broken down by digestion with sulphuric acid.

A solution containing, in 100 c.c., 25 grams of trigalactangeddic acid and 3 grams of sulphuric acid, was heated at 98° in a water-bath, and the digestion continued for two hours. The liquid was then cooled, neutralised with baryta-water, and the barium sulphate separated by filtration. When the gum acids are degraded to the extent they are under under these circumstances, the barium sulphate is easily separated, and the solution filters clear. The filtrate was concentrated in a vacuum to a syrup, and alcohol (0 82) added as long as a precipitate was produced; this was freed from sugars by repeated dissolution in water and precipitation with alcohol. It contained the barium salt of the degraded gum acid; the sugars were in the alcoholic solutions, which, however, contained also some barium salt. This was eliminated by repeatedly evaporating to a syrup in a vacuum and taking up with strong alcohol. The final solution was freed from alcohol by distillation, and the optical activity of the sugars determined. Sp. gr. of solution 1·03214; optical activity in a 200-mm. tube $\alpha_D = +12·50°$; hence

$$[\alpha]_D = +74·9°.$$

This solution was not free from barium, and as the amount of sugar in 100 c.c. was inferred from the sp. gr., the specific rotatory power obtained for the sugars must be too low. It was again evaporated to a syrup, and treated with hot alcohol, which dissolved it all except a small portion rich in barium. The clear alcoholic solution deposited, on standing, a small crop (*a*) of crystals. This was separated, and the alcohol distilled off. The syrup thus obtained was dissolved in its own weight of dry methyl alcohol; this solution yielded a large crop (*b*) of crystals on standing. A further crop (*c*) was obtained from the mother liquids. Determinations of those three crops of crystals were made with the following results:—

2·570 grams *a* crop gave 100 c.c., sp. gr. 1·00988; this, in a 200-mm. tube, gave a rotation $\alpha_D = +4·0°$.

3·413 grams *b* crop gave 100 c.c., sp. gr. 1·01314; this, in a 200-mm. tube, gave a rotation $\alpha_D = +5·50°$.

1·620 grams *c* crop gave 100 c.c., sp. gr. 1·00624; this, in a 200-mm. tube, gave a rotation $\alpha_D = +2·63°$.

The crystals were anhydrous.

From these figures we have, for the specific rotatory power of the three crops:—

a. $[\alpha]_D = +77·8°$.
b. $[\alpha]_D = +80·6°$.
c. $[\alpha]_D = +81·2°$.

The optical activity of galactose at the temperature and degree of average concentration of these observations is

$$[\alpha]_D = +81·4°,$$

and, as the crops of crystals have all the same habitus as that sugar, and as they yield mucic acid on oxidation with nitric acid, they consist of galactose in a moderately pure state. On recrystallisation from water, a product was obtained having the exact crystalline form and specific rotatory power of galactose. Besides this sugar and a trace of barium salt, there was only a very small quantity of uncrystallisable syrup of low optical activity in the alcoholic solutions. Whether this syrup is the result of the action of the acid on the sugar, which is very probable, as I have shown that arabinose and, as we know, dextrose are acted upon in the same way, or on the gum acid, I must leave undecided for the present.

On attempting to purify the gum acid or acids of the barium salt, as far as possible, by dialysis with hydrochloric acid, it was found that the greater portion of the gum acid diffused, only a small and somewhat coloured portion being left on the dialyser. This was too opalescent to admit of an optical determination. It was divided into four fractions, and the barium salts prepared of the second (α) and fourth (β). These were analysed:—

0·746 gram (α) gave 0·114 gram $BaSO_4$.
0·522 „ (β) „ 0·079 „

Numbers corresponding to:—

α = 10·03 per cent. BaO.
β = 9·94 „ „

The fraction, therefore, left on the dialyser is a fairly pure homogeneous substance. As, however, this was only a small portion of the acid produced by the degradation, a further quantity of trigalactangeddic acid was acted upon, in the same way as described above. The sugar in the alcoholic solution was found to be galactose. The barium salt was divided into eight fractions: 1 being the most insoluble. An optical activity, sp. gr., and barium oxide determination was made of each of these; 1, being a small and rather unsatisfactory fraction, was rejected:—

0·563 gram	2	gave	0·070 gram	$BaSO_4$.
0·426 „	3	„	0·096	„
0·182 „	4	„	0·039	„
0·536 „	5	„	0·114	„
0·803 „	6	„	0·180	„
0·732 „	7	„	0·110	„
0·698 „	8	„	0·082	„

2·214 grams 2 gave 100 c.c. solution, sp. gr. = 1·01048, which, in a 200-mm. tube, deviated the ray $\alpha_D = +1·4°$.
1·706 grams 3 gave 100 c.c. solution, sp. gr. = 1·00854, which, in a 200-mm. tube, deviated the ray $\alpha_D = +1·92°$.
2·146 grams 5 gave 100 c.c. solution, sp. gr. = 1·01052, which, in a 200-mm. tube, deviated the ray $\alpha_D = +2·20°$.
3·212 grams 6 gave 100 c.c. solution, sp. gr. = 1·01658, which, in a 200-mm. tube, deviated the ray $\alpha_D = +3·75°$.
2·928 grams 7 gave 100 c.c. solution, sp. gr. = 1·01370, which, in a 200-mm. tube, deviated the ray $\alpha_D = +3·48°$.
2·794 grams 8 gave 100 c.c. solution, sp. gr. = 1·01270, which, in a 200-mm. tube, deviated the ray $\alpha_D = +3·15°$.

From these numbers, we have the following factors:—

	Per cent. BaO.	Sp. rot. power for acid free from BaO.	D.
2........	8·31	$[\alpha]_D = +34·5°$	4·73
3........	14·79	$[\alpha]_D = +65·5°$	5·01
4........	14·07	—	—
5........	13·94	$[\alpha]_D = +60·0°$	4·90
6........	14·72	$[\alpha]_D = +68·4°$	5·16
7........	9·87	$[\alpha]_D = +65·9°$	4·68
8........	7·71	$[\alpha]_D = +61·1°$	4·54

A further treatment of fraction 2 showed the high activity and low percentage of barium oxide to be due to a galactose-yielding body, probably *galacton*, the saccharon of galactose, contaminating a gum acid containing slightly over 10 per cent. BaO. Fractions 3, 4, 5, and 6 are clearly a mixture of two or more barium salts, contaminated probably with sugar; and fractions 7 and 8 are gum acid salts, evidently containing sugar. The latter were mixed, dissolved in water, and carefully purified by repeated solution and reprecipitation with alcohol. The alcoholic solutions were all collected, concentrated to a syrup, and dissolved in a small quantity of methyl alcohol. On standing, the solution crystallised. The sugar thus obtained was found to have an optical activity

$$[\alpha]_D = +81{\cdot}1^\circ,$$

and to yield mucic acid on oxidation with nitric acid, so that it was pure galactose. The purified barium salt was divided into two fractions, one of which was analysed. It yielded 13·90 per cent. BaO, and had an optical activity for organic acid

$$[\alpha]_D = +62{\cdot}5^\circ.$$

It is clear, therefore, that the barium salts in fractions 7 and 8 were of the same nature as those in the other fractions, and that it is difficult to separate these salts from sugar.

The whole of the purified fractions were mixed and again submitted to careful treatment with alcohol. Some of the more soluble fractions were found to contain between 14 and 15 per cent. of BaO, and a more insoluble fraction was obtained, which, on analysis, yielded the following results:—

0·702 gram dry substance gave 0·163 gram $BaSO_4$.
2·808 grams dry substance gave 100 c.c. solution, sp. gr. = 1·01410; and this, in a 200-mm. tube, deviated the ray $\alpha_D = +2{\cdot}95^\circ$.

These numbers lead to the factors

15·25 per cent. BaO; $[\alpha]_D = +62{\cdot}0^\circ$ for acid free from BaO.

On referring to Part I of this paper (Trans., 1884, 45, 46), we find a barium salt described; it was obtained under the same conditions from arabic acid as this salt was prepared from the gedda gum acid, containing 15·59 per cent. BaO, but having little or no optical activity. The acids neutralise practically the same quantity of barium oxide, but they are not identical, as is shown by the difference in the optical activity. Do they contain the same proportion of carbon and hydrogen? The salt of the arabic series gave a percentage agreeing with the formula $C_{29}H_{48}O_{27},BaO$.

The portion of the geddic salt of which an analysis is given above was mixed with all the fractions from the same source containing 14 to 15 per cent. BaO, and having an optical activity varying between $[\alpha]_D = +62^\circ$ and $+66^\circ$, and again purified by repeated treatment with alcohol. The salt thus obtained was burnt in the usual way in a current of oxygen.

I. 0·3290 gram dry barium salt gave H_2O = 0·147 gram, CO_2 = 0·417 gram. and $BaCO_3$ = 0·0665* gram.

II. 0·3732 gram dry barium salt gave H_2O = 0·168 gram, CO_2 = 0·474 gram, and $BaCO_3$ = 0·0752 gram.

From these numbers we have:—

	Found.		Theory for
	I.	II.	$C_{29}H_{48}O_{27}BaO$.
C per cent.......	35·83	35·83	35 47
H „	4·96	5·00	4·89
BaO per cent...	15·70	15·66	15·59

These numbers agree sufficiently closely to warrant the application of the arabinosic formula to the geddic derivative. The latter I propose to call *β-geddinosic acid.*

Further, in dealing with the arabic series, I showed (*loc. cit.*) that an acid having the composition $C_{23}H_{38}O_{22}$ was obtained as the result of the digestion of arabic acid for three or four hours with sulphuric acid. An acid of this composition, no doubt, is also obtained by treating trigalactangeddic acid or the higher acids in the same way. I have not thought it necessary to isolate the acid, but the evidence I obtained of its existence is conclusive. One of the natural gum acids, in fact, triarabinantrigalactangeddic acid, was digested in the usual way with sulphuric acid for three hours. The transformed solution was neutralised with baryta-water, the barium sulphate filtered off, and the filtrate concentrated. The precipitate with alcohol was freed from sugar as much as possible by treatment with alcohol, and then divided into two fractions, *a* and *b*; on analysis, these yielded the following results:—

0·835 gram of *a*, dried as usual, gave 0·217 gram $BaSO_4$.
1·312 „ *b* „ „ 0·338 „
3·340 „ *a* „ „ 100 c.c. solution, sp. gr. 1·01706, and this solution gave a rotation $\alpha_D = +3·80°$ in a 200-mm. tube.

a = 17·1° per cent. BaO; $[\alpha]_D = +68·2°$ for free acid.
b = 16·9° „ „ „ „
Theory for $C_{23}H_{38}O_{22}$,BaO, 18·68 per cent. BaO.

There can be no doubt that a salt of this composition could be obtained by carefully fractionating *a* or *b*, but when we take the facts already established into account, it seemed to me unnecessary to prepare the salt in the pure state. The α fraction is a mixture of barium β-geddinosate and the barium salt of the low acid in about equal parts; taking the percentage of barium as the indicator, the optical activity of the low acid, which I propose to call *geddic acid*, would be $[\alpha]_D = +71°$ about. The corresponding arabic acid has little or no optical activity; the acids from the two sources are isomeric, they differ in optical activity.

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* There was no increase in weight when the residue in the boat after burning the BaO salts was treated with ammonium carbonate.

We may now turn to the acid obtained as the first marked resting stage of the action of sulphuric acid on the natural gum acids, namely, trigalactangeddic acid, represented by the symbol Tg, and described above, and inquire what relation this acid holds to the final one, the existence of which I have just indicated, and which I have called geddic acid. As I showed that barium trigalactangeddate contains 8·4—8·5 per cent. of barium; that by the action of sulphuric acid it yields geddic acid, $C_{23}H_{38}O_{22}$, and that no other product is formed except galactose, it is clear that the higher acid must be some compound of galactose, or a galactose-yielding substance, with geddic acid. Taking $C_{12}H_{20}O_{10}$ to represent a hypothetical galactan, $3C_{12}H_{20}O_{10},C_{23}H_{38}O_{22},BaO$, that is, TgBaO, would represent the constitution of the salt. This formula requires 8·54 per cent. BaO, against the 8·4—8·5 per cent. found; hence the term *trigalactangeddic acid.*

If this is the real relationship existing between the two acids, an elementary analysis of trigalactangeddic acid, or of its barium salts, should yield results confirmatory of the hypothesis. Combustions were made of several preparations of the barium salts with the following results:—

0·2820 gram I in dry state gave H_2O = 0·141 gram, CO_2 = 0·415 gram, and $BaCO_3$ = 0·0312 gram.
0·3551 gram II in dry state gave H_2O = 0·172 gram, CO_2 = 0·528 gram, and $BaCO_3$ = 0·0391 gram.
0·2126 gram III in dry state gave H_2O = 0·104 gram, CO_2 = 0·312 gram, and $BaCO_3$ = 0·0235 gram.
0·2863 gram IV in dry state gave H_2O = 0·144 gram, CO_2 = 0·424 gram, and $BaCO_3$ = 0·0317 gram.
0·3585 gram V in dry state gave H_2O = 0·174 gram, CO_2 = 0·528 gram, and $BaCO_3$ = 0·0390.

These results calculated for the free acid are:—

	I.	II.	III.	IV.	V.	Theory for $3C_{12}H_{20}O_{10},C_{23}H_{38}O_{22}$.
C....	44·64	45·02	44·50	44·92	44·62	43·2
H...	6·07	5·85	5·95	6·11	5·89	5·98

The BaO in the salt being—

	I.	II.	III.	IV.	V.
BaO .	8·59	8·56	8·59	8·60	8·45

The carbon found is much higher than that required by this theory; the hydrogen affords no marked evidence, but taking the general results of hydrogen determinations into consideration, the numbers obtained are too low, on the whole, for the theory. It is clear, therefore, that the relationship between geddic acid and trigalactangeddic acid is not that mentioned above. If, however, we suppose that each $C_{12}H_{20}O_{10}$ group hydrolysed occupied the place of a water molecule, H_2O, in $C_{23}H_{38}O_{22}$ we have a compound $3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19}$, which requires

C............	44·70
H............	5·81

numbers agreeing perfectly with those found. $3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19},BaO$ requires 8·80 per cent. BaO, a number agreeing sufficiently closely with those found, especially when it is considered that the acid can only with difficulty be freed from magnesium and potassium oxides, which take the place of a portion of the barium oxide.

It is, therefore, clear that the formula of trigalactangeddic acid is $3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19}$, and that the equation

$$3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19} + 9H_2O = \underset{\text{Geddic acid.}}{C_{23}H_{38}O_{22}} + \underset{\text{Galactose.}}{6C_6H_{12}O_6}$$

represents the final action of sulphuric acid upon it.

I may here point out that in dealing with the breaking down of arabic acid, I showed that, after a certain stage of the degradation, the breaking down was accompanied with the fixation of more water than was required to convert a $C_6H_{10}O_5$ or a $C_{12}H_{20}O_{10}$ compound into a $C_6H_{12}O_6$ one, in exactly the same way as is here indicated.

Between trigalactangeddic acid and geddic acid, I have been able to obtain evidence of the existence of only two acids, namely, the acid left upon the dialyser, the barium salt of which contained 10·03 and 9·94 per cent. of barium oxide, and the acid of the fractions containing between 14 and 15 per cent. BaO. Two preparations of the barium salt of the former were analysed with the following results:—

0·3512 gram I dry salt gave H_2O = 0·183 gram, CO_2 = 0·500 gram, and $BaCO_3$ + 0·0469 gram.

0·3931 gram II dry salt gave H_2O = 0·202 gram, CO_2 = 0·561 gram, and $BaCO_3$ = 0·520 gram.

	Found.		Theory for
	I.	II.	$2C_{12}H_{20}O_{10},C_{23}H_{34}O_{20},BaO$.
C	39·60	39·75	39·40
H.......	5·79	5·71	5·16
BaO	10·37	10·28	10·61

These numbers agree sufficiently well to support the theory; the agreement would, of course, be closer if the carbon and hydrogen were calculated on the acid free from ash. This acid I call *digalactangeddic acid.*

The second acid, the barium salt of which contains between 13 and 14 per cent. BaO, I call *monogalactangeddic acid*, because

$$C_{12}H_{20}O_{10}C_{23}H_{36}O_{21}BaO$$

requires 13·66 per cent. BaO. The optical activity of this acid would be somewhere about $[\alpha]_D = +58—60°$.

Having thus far securely established the relationship existing between the final acid, geddic acid, and trigalactangeddic acid, we may return to inquire whether or not the relationship of the natural gum acids to one another, and to trigalactangeddic acid, is exactly as was indicated by the composition of the barium salts. This composition indicated that the natural gum acids were compounds of trigalactangeddic acid with hypothetical arabinan, $C_{10}H_{16}O_8$, so that, substituting $3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19}$ for Tg, the formula of tetrarabinantrigalactangeddic acid would be $4C_{10}H_{16}O_8,3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19}$. Is this so? Combustions were made of four preparations of this acid, namely, two calcium salts and two free acids, with the following results:—

I. 0·2481 gram dry CaO salt gave H_2O = 0·134 gram, CO_2 = 0·398* gram, $CaCO_3$ = 0·0094† gram.

II. 0·3315 gram dry CaO salt gave H_2O = 0·174 gram, CO_2 = 0·536* gram, $CaCO_3$ = 0·0125.†

III. 0·2641 gram dry acid gave H_2O = 0·143 gram, CO_2 = 0·437 gram.

IV. 0·3716 gram dry acid gave H_2O = 0·202 gram, CO_2 = 0·616 gram.

	Found.				Theory for
	I.	II.	III.	IV.	$4C_{10}H_{16}O_8,3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19}$.
C	44·71	45·05	45·13	45·21	45·00
H	6·13	5·96	6·52	6·04	5·91
					$4C_{10}H_{16}O_8,3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19},CaO$.
CaO ..	2·12	2·11	—	—	2·08

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* This number includes the CO_2 weighed and the CO_2 as $CaCO_3$ in boat, the boat being weighed before treatment of ash with ammonium carbonate.

† After treatment of ash with ammonium carbonate.

These numbers prove conclusively that the relationship indicated by the barium salts is that existing between trigalactangeddic acid and tetrarabinantrigalactangeddic acid, that unlike the group yielding galactose, the group from which the arabinon and arabinose are derived is hydrated, without hydration of the derived acid taking place at the same time. The facility with which the arabinan is removed, and the difficulty with which the galactan-containing acids are broken down, show clearly, too, that the bond of union in both cases cannot be the same.

The barium salt of tetrarabinantrigalactangeddic acid yielded 5·33—5·42 per cent. BaO; the formula

$$4C_{10}H_{16}O_{6},3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19},BaO$$

requires 5·47 per cent. BaO.

The barium salt of triarabinantrigalactangeddic acid yielded 5·9—6·07 per cent. BaO; the formula

$$3C_{10}H_{16}O_{8},3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19},BaO$$

requires 6·04 per cent. BaO.

The barium salt of diarabinantrigalactangeddic acid yielded 6·6—6·7 per cent. BaO; the formula

$$2C_{10}H_{16}O_{8},3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19},BaO$$

requires 6·75 per cent. BaO.

The barium salt of monarabinantrigalantangeddic acid yielded 7·3—7 6 per cent. BaO; the formula [$C_{10}H_{16}O_{8},3C_{12}H_{20}O_{10},C_{23}H_{32}O_{19},BaO$] requires 7·65 per cent. BaO.

In all these cases, the theory agrees well with the numbers found; taking this into account, as well as the general facts demonstrated in this paper, it is clearly established that these formulæ, attributed to the natural gum acids and to the products of their degradation, are highly probable. The gum is a mixture of the calcium, magnesium, and potassium salts of these acids in various proportions, together with a small quantity of proteïd as mentioned above.

The evidence afforded by the constitution of this gum, and of the acids it contains, seems to me to point distinctly to these bodies as *materials*—matter being built up, and to be employed in building up, rather than as *débris*—matter produced by the breaking down of substances of greater complexity. If, too, they were *débris*, we can have no doubt that the gum would contain other products of the degradation. This we find is not the case, for, although there is undoubtedly a trace of sugar present, there is not anything like sufficient to account, for example, for the degradation of tetrarabinantrigalactangeddic acid to monarabinantrigalactangeddic acid. It is not possible to say whether the nitrogenous matter is *débris* or material, for it has been but slightly examined. in consequence of its being present in very small quantity, and of the difficulty of arriving at any simple factor of it which would serve as a criterion of its homogeneity or purity.

This work, so far, is complete in itself, for it gives us a clear insight into the constitution of a dextrorotatory gum; but I felt that the paper would not be complete unless I was able to show that all the dextrorotatory gums were like the one described, or held some well-defined relationship to it. The investigation was commenced in 1883, and in 1887, before I was able to quite satisfy myself upon many points described above, the supply of the A sample of gum became exhausted. I had, therefore, to seek a fresh supply. I applied to the firm from whom the first sample was obtained, but a few experiments with the sample furnished showed me that I had an altogether different gum in my hands. It became necessary, therefore, to submit the fresh sample to pretty well as full an investigation as the first. This I undertook the more readily, as I hoped the results would confirm and complete those already described.

Sample of Gedda Gum B.

Physically there was no apparent difference between this sample and the A sample. The colour was the same in both, and there was no material difference in the shape or size of the pieces. If anything, the darker pieces of the B sample were more contaminated with bark and sand than those of the A sample. Neglecting these pieces, the sample was easily divisible into B *a*, light glassy pieces, B *b*, dark-ruby pieces, and B *c*, deep-reddish ones. An optical activity determination of each of these divisions was made with the following results; the sp. gr. of the solution was employed as the indicator of the amount of substance in solution.

$$\begin{aligned} \mathrm{B}\,a.\ [\alpha]_D &= +83{\cdot}4^\circ \\ \mathrm{B}\,b.\ [\alpha]_D &= +80{\cdot}7^\circ \\ \mathrm{B}\,c.\ [\alpha]_D &= +68{\cdot}9^\circ. \end{aligned}$$

These numbers show that the second sample of gum is not the same as the first, and that, like it, it is not homogeneous.

Ash determinations were also made:—

1·091 grams B *a* gave 0·022 gram ash after treatment with $(NH_4)_2CO_3$.

5·678 grams B *b* gave 0·107 gram ash after treatment with $(NH_4)_2CO_3$.

5·466 grams B *c* gave 0·093 gram ash after treatment with $(NH_4)_2CO_3$.

Hence B a = 2·0 per cent. ash.
B b = 1·89 „
B c = 1·70 „

On comparing these percentages with those obtained for the A sample, we find there is much less ash in the B sample. The reason of this will be clear later on. The constitution of the ash in both samples was, however, practically the same, namely, calcium carbonate in greater part, with a small quantity of potassium and magnesium carbonates, and a trace of silicic and phosphoric acids.

It was no use to attempt to fractionate the gum mechanically, because I found that even pieces of exactly the same colour contained more than one gum acid; hence, as in the case of the A sample, I had recourse to the precipitation method. In dealing with it, however, a difficulty presented itself; a considerable quantity of the gum acid was soluble in strong alcohol. When a strong solution, one of water to one of gum, was acidified with hydrochloric acid, and the least soluble fraction thrown out by the addition of alcohol, of sp. gr. 0·85, further addition of this alcohol to the clear solution did not precipitate nearly the whole of the gum acid; this was only effected on neutralisation with milk of lime; the calcium salt of the most soluble acid was then precipitated. Proceeding in this way, the gum was divided into four fractions: a, the least soluble, was thrown out first, b was precipitated by a further addition of alcohol to the clear solution, c was next thrown out, and d, the most soluble fraction, was precipitated only as lime salt on neutralising with milk of lime.

Fractions a and b contained much nitrogenous matter; they were again mixed and divided into fractions a_1, a_2, and a_3, the first being the least soluble. After these substances had been dried, they were insoluble in water, and had to be dissolved in dilute soda to admit of an optical observation. They were all strongly acid to litmus, hydrochloric acid being proved to be absent. In alkaline solution the optical activity was found to be

$$a_1.\ [\alpha]_D = +38^\circ$$
$$a_2.\ [\alpha]_D = +38^\circ$$
$$a_3.\ [\alpha]_D = +46^\circ.$$

Neither fraction was free from nitrogenous matter. On further treating a_3, a soluble fraction was obtained, free from nitrogen, the optical activity of which was

$$[\alpha]_D = +80—83^\circ,$$

the more insoluble portion having an optical activity not far removed from that of a_1 and a_2. I must leave to a future occasion a description of my attempts to purify these substances, and an account of the nitrogenous matter they contain. I may, however, state here, that the nitrogenous matter is of the nature of a proteïd, and that it gives the following reactions :—

I. It is diastatic, that is, it dissolves starch like malt diastase.* It does not invert sucrose.

II. When precipitated and dried, it does not dissolve in water to a clear solution, yet the greater portion of the substance is evidently soluble.

III. It dissolves easily in soda or potash to a perfectly clear solution, with the production of a slight brown colour, if the alkali is in excess. On adding acid to the strong solution, no cloudiness is produced, but the colour disappears.

IV. No precipitate is produced by boiling the acid or alkaline solutions.

V. An alkaline solution yields a beautiful purple colour on the addition of a drop or two of Fehling's solution; the colour is much intensified on the application of heat. There is no reduction, except on long boiling, and then it is only slight, the solution still retaining its purple or rose colour.

VI. When boiled with strong nitric acid, it yields a dark-brown solution; potash discharges the colour to some extent, and produces a flocculent precipitate.

VII. When boiled with nitric acid not sufficiently strong to give rise to nitrous fumes, a yellowish-red solution is obtained, which on cooling deposits a yellowish, flocculent precipitate.

VIII. With Millon's reagent it yields a rose-pink coloration, which becomes yellow on adding an excess of the reagent.

IX. In strong acetic acid solution, no precipitate is produced on the addition of potassium ferrocyanide.

We have again to turn to the portions of the gum which were found to be free from nitrogen. Fraction *c* was found to have an optical activity

$$[\alpha]_D = +90^\circ,$$

and *d*

$$[\alpha]_D = +102^\circ.$$

Proceeding after the manner described in dealing with the A sample of gum, I found it possible to divide the portion of this gum free from nitrogen into four fractions, viz. :—

A. $[\alpha]_D = +107—110^\circ$,
B. $[\alpha]_D = +99—101^\circ$,
C. $[\alpha]_D = +89—91^\circ$,
D. $[\alpha]_D = +80—83^\circ$.

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* This reaction was observed for the whole gum.

A is the most, and D the least, soluble fraction. The B fraction constituted the greater portion of the gum free from nitrogen; A and D were small fractions.

As mentioned above, the high solubility of these gum acids in alcohol was a great obstacle to their separation. The aqueous solution had to be made concentrated, and, when alcohol was added, it not unfrequently happened that a portion of a higher rotating fraction was precipitated, and a portion of a lower rotating one held in solution; it was thus exceedingly difficult to effect a separation. Feeling, however, that this was chiefly due to too rapid precipitation, and to the concentration of the solution, I found that by guarding against these sources of complication, I was able to so arrange matters as to ensure that the most soluble fraction was the most optically active, and did not contain any substance of less optical activity than the most soluble portion of the fraction next in solubility. There was very great difficulty in separating these acids from lime; this necessitated taking the percentage of lime in the neutral lime salts as an indication of the neutralising power.

A *fraction*.—The most soluble fraction was dialysed until as free from ash as possible; it was then divided into three parts: A_1, free acid; A_2, converted into lime salt; and, A_3, into baryta salt. These were analysed, with the following results:—

2·773 grams free acid gave 100 c.c. solution, sp. gr. 1·01040, and this solution gave a rotation $\alpha_D = +5·97°$ in a 200-mm. tube.

0·765 gram dry calcium salt gave 0·015 gram $CaCO_3$.

3·060 grams dry calcium salt gave 100 c.c., sp. gr. 1·01160, and this solution gave a rotation $\alpha_D = +6·6°$ in a 200-mm. tube.

0·658 gram dry barium salt gave 0·028 gram $BaSO_4$.

2·634 grams dry barium salt gave 100 c.c. solution, sp. gr. 1·1040, and this solution gave a rotation $\alpha_D = +5·5°$.

From these numbers we have the following factors:—

Free acid	$[\alpha]_D = +107·6°$,
Free acid in calcium salt..	$[\alpha]_D = +109·0°$,
„ in barium salt ..	$[\alpha]_D = +107·4°$.

CaO in calcium salt = 1·1 per cent.
BaO in barium salt = 2·79 per cent.

B *fraction*.—This being the largest portion, a thorough fractionation was made of it. All the preparations with an optical activity $[\alpha]_D = +100$ (about) were mixed, a small, less soluble portion taken out at one end, a very small, more soluble one at the other, and the great bulk of the fraction, after being dialysed and repeatedly precipitated, was divided into three fractions: B_1, B_2, and B_3, the first bring the least soluble.

B_1. The free acid and barium and calcium salts of this fraction were examined.

3·596 grams free acid, dried as usual, gave 100 c.c. solution, sp. gr. 1·01318, and this solution, in a 200-mm. tube, gave a rotation $\alpha_D = +7·03°$.

0·899 gram dry acid gave 0·0015 gram ash.[*]

0·649 gram dry barium salt gave 0·0394 gram $BaSO_4$.

2·596 " " " 100 c.c. solution, sp. gr. 1·01034, and this solution, in a 200-mm. tube, gave a rotation $\alpha_D = +4·98°$.

0·818 gram dry calcium salt gave 0·020 gram $CaCO_3$.

3·274 " " " 100 c.c. solution, sp. gr. 1·01248, and this solution, in a 200-mm. tube, gave a rotation $\alpha_D = +6·63°$.

B_2. This fraction was examined as calcium salt.

0·732 gram dry calcium salt gave 0·018 gram $CaCO_3$.

2·928 grams " " 100 c.c. solution, sp. gr. 1·01132, and this solution, in a 200-mm. tube, gave a rotation $\alpha_D = +5·82°$.

B_3. This was also examined as calcium salt.

0·717 gram dry calcium salt gave 0·018 gram $CaCO_3$.

2·870 grams " " 100 c.c. solution, sp. gr. 1·01110, and this solution gave a rotation $\alpha_D = +5·70°$ in a 200-mm. tube.

From these data we have the following factors:—

Free acid, B_1.	$[\alpha]_D$ = +97·7°;	D = 3·67;	ash = 0·17	per cent.[†]
Barium salt, "	$[\alpha]_D$[‡] = +99·3°;	D = 3·98;	BaO = 3·99[§]	"
Calcium salt, "	$[\alpha]_D$[‡] = +98·9°;	D = 3·81;	CaO = 1·37	"
Calcium salt, B_2.	$[\alpha]_D$[‡] = +100·8°;	D = 3·87;	CaO = 1·38	"
Calcium salt, B_3.	$[\alpha]_D$[‡] = +100·8°;	D = 3·87;	CaO = 1·41	"

The specific rotatory power and density of the free acid are low, and I may say that this is a general rule when these acids are examined in the free state; I have reason to believe that this is due to the retention of alcohol by the free acid, probably as an ether. The true divisor, D, of the free acid I estimate at 3·75, and if the optical activity observed be corrected by this factor, the specific rotatory power of the acid will be $[\alpha]_D = +100°$. All the factors agree so well, that there can be no doubt that the B fraction is a homogeneous substance.

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[*] Proved to be calcium carbonate.

[†] Calcium carbonate.

[‡] The specific rotatory power is calculated for the organic portion of the salt.

[§] Corrected for ash (calcium carbonate).

C *fraction.*—All the pieces with a specific rotatory power $[\alpha]_D$ = +90° (about) were mixed, small fractions taken out above and below as in the preceding case, and the large, middle portion, after dialysis and repeated precipitations, was divided into three fractions, C_1, C_2, and C_3, the latter being the most soluble. The calcium salt of each of these was examined.

C_1. 0·826 gram dry calcium salt gave 0·025 gram $CaCO_3$.
3·306 grams „ „ 100 c.c. solution, sp. gr. 1·01278, and this solution, in a 200-mm. tube, gave a rotation α_D = +5·85°.

C_2. 0·766 gram dry calcium salt gave 0·023 gram $CaCO_3$.
3·066 grams „ „ 100 c.c. solution, sp. gr. 1·01186, and this solution, in a 200-mm. tube, gave a rotation α_D = +5·45°.

C_3. 0·794 gram dry calcium salt gave 0·022 gram $CaCO_3$.
3·178 grams „ „ 100 c.c. solution, sp. gr. 1·01230, and this solution, in a 200-mm. tube, gave a rotation α_D = +5·72°.

These data lead to the following factors :—

C_1. $[\alpha]_D$ = +90·0° ;* calcium salt, D = 3·86 ; CaO = 1·70 per cent.
C_2. $[\alpha]_D$ = +90·5° ; „ D = 3·87 ; CaO = 1·70 „
C_3. $[\alpha]_D$ = +91·1° ; „ D = 3·87 ; CaO = 1·60 „

These numbers prove conclusively that the C fraction is a homogeneous substance. Other fractionations of other preparations of this fraction were made with results agreeing well with those. I may give another set of determinations.

A free acid, $[\alpha]_D$ = 90°, was divided into two fractions, C_4 and C_5, the former being the least soluble, and of these calcium salts were prepared and analysed.

C_4. 0·778 gram dry calcium salt gave 0·024 gram $CaCO_3$.
3·113 grams „ „ 100 c.c. solution, sp gr. 1·01214, and this solution gave a rotation α_D = +5·55° in a 200-mm. tube.

C_5. 0·575 gram dry calcium salt gave 0·017 gram $CaCO_3$.
2·300 grams „ „ 100 c.c. solution, sp.gr. 1·0090, and this solution gave a rotation α_D = +4·15° in a 200-mm. tube.

From these data the following factors are calculated :—

C_4. $[\alpha]_D$* = +90·7 ; calcium salt, D = 3·90 ; CaO = 1·73 per cent.
C_5. $[\alpha]_D$ = +91·8 ; „ D = 3·91 ; CaO = 1·66 „

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* The specific rotatory power is calculated for the organic portion of the salt.

The agreement of these numbers amongst themselves and with those obtained in the previous experiments is perfectly satisfactory.

These two fractions were again mixed, dissolved in a little water and hydrochloric acid, and then alcohol added; the precipitate was redissolved and reprecipitated until it was free from hydrochloric acid. A barium salt of a portion of this was prepared, and the free acid itself was dried; both preparations were examined.

2·783 grams dry free acid containing only traces of ash, gave 100 c.c. solution, which, in a 200-mm. tube, gave a rotation $\alpha_D = +5·0°$.

0·733 gram dry barium salt gave 0·047 gram $BaSO_4$.

2·934 grams „ „ 100 c.c. solution, sp. gr. 1·01186, and this solution, in a 200 mm.-tube, gave a rotation $\alpha_D = +5·05°$.

From these data—

Free acid, $[\alpha]_D = +89·8°$;

Barium salt, $[\alpha]_D = +89·9°$;* D = 4·04; BaO = 4·21 per cent.

D fraction was, as I have said, small, and, taking into consideration the fact that its specific rotatory power holds pretty well the same relation to that of the C fraction as the latter holds to B and B to A, it seemed to me fair to conclude that this acid is one of a series, and if I can establish a relationship between A and B and B and C, it will not be unreasonable to conclude that the same relationship holds between C and D. The optical activity of this fraction may be taken as $[\alpha]_D = +80—82°$.

On comparing the factors of the members of this series with those of the members of the A sample of gum, we find that, apparently, these acids are higher members of the A sample series, the acid with highest optical activity $[\alpha]_D = +59°$, and with a calcium salt containing 2·1 per cent. lime, tetrarabinantrigalactangeddic, is separated seemingly by an absent acid $[\alpha]_D = +70°$ (about), from the lowest member, $[\alpha]_D = +80—83°$, of the B sample group; in other words, a *pent*arabinantrigalactangeddic acid would appear to be absent, and a *hex*arabinantrigalactangeddic appears as the first and lowest member of the B sample series; the next highest member, $[\alpha]_D = +90°$, being *hept*arabinantrigalactangeddic acid, and so on for the $[\alpha]_D = +100°$ and the $[\alpha]_D = +110°$ acids. This would seem to be borne out, too, by the decreasing amount of lime in the calcium salts, and, also, by the increasing solubility in alcohol in the higher acids. If this is the relationship that exists, the first resting stage in the action of sulphuric acid on the acids of the B series should be the same acid as that which was found in dealing with the A series, namely, trigalactangeddic acid.

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* The specific rotatory power is calculated for the organic portion of the salt.

A portion of the B fraction above described was acted upon with sulphuric acid for 20 minutes, in the usual way, and the resulting solution treated with alcohol after the manner already described. The portion insoluble in alcohol was purified from sugar by further treatment with alcohol, then dialysed with hydrochloric acid until free from ash, and further purified by removing a slight, most soluble, and least soluble portion with alcohol. The middle, and by far the greatest portion, was then divided into two fractions, α and β; these were converted into barium salts.

Bα. 0·669 gram barium salt, dried as usual, gave 0·071 gram $BaSO_4$.
2·678 grams gave 100 c.c. solution, sp. gr. 1·01182, and this solution, in a 200-mm. tube, gave a rotation $\alpha_D = +1·0°$.

Bβ. 0·770 gram barium salt, dried as usual, gave 0·084 gram $BaSO_4$.
3·080 grams gave 100 c.c. solution, sp. gr. 1·01370, and this solution, in a 200-mm. tube, gave a rotation $[\alpha]_D = +1·1°$.

Hence, Bα. $[\alpha]_D = +20·1°$,
Bβ. $[\alpha]_D = +19·2°$.

Bα = 6·97 per cent. BaO; D = 4·41,
Bβ = 7·17 „ BaO; D = 4·45.

The free acid, $[\alpha]_D = +19·2$, was again acted upon for 10 minutes with sulphuric acid, and the resulting solution treated as usual with alcohol. Very little action had taken place, as the alcohol contained only a very small quantity of sugar. The precipitate was washed and purified, and a barium salt prepared of it.

0·658 gram dry barium salt gave 0·070 gram $BaSO_4$.
2·632 grams „ „ 100 c.c. solution, sp. gr. 1·01186, and this solution, in a 200-mm. tube, gave a rotation $\alpha_D = +0·95°$.

Hence 6·99 per cent. BaO; $[\alpha]_D = +19·4°$; D = 4·50.

Fraction C, $[\alpha]_D = +90°$, was acted upon in the same way with exactly the same results.

Many other transformations were made without any material alteration in the character of the product. In all cases, the acid obtained had an optical activity $[\alpha]_D = +20°$ (about), and gave a barium salt which yields 7·2—7·4 per cent. BaO. It is therefore certain that this acid is a resting stage in the action of sulphuric acid on the acids of the B fraction of the B sample of gedda gum.

Before proceeding further, we may examine the alcoholic solution, and determine if arabinon and arabinose are the only other products of the degradation. It was neutralised with baryta-water, the barium sulphate removed by filtration, and the filtrate evaporated to a syrup in a vacuum. This was treated with strong alcohol, which, in all cases, dissolved it all except a small portion of the barium salt of a gum acid, a portion of which was also thrown down with the barium sulphate on neutralising the alcoholic solution; this was separated by treating the sulphate with boiling water and filtering; it will be returned to later on. The alcoholic solution was again evaporated to a syrup which, on standing a few days, yielded a large crop of crystals (*a*), a second (*b*), third (*c*), and fourth (*d*) crop were obtained, and, finally, a small portion of mother liquid (*e*) was left. An optical activity determination was made of all these crops.

$(a.)\ [\alpha]_D = +108{\cdot}9^\circ \quad c = 3{\cdot}122,$
$(b.)\ [\alpha]_D = +104{\cdot}6^\circ \quad c = 4{\cdot}062,$
$(c.)\ [\alpha]_D = +102{\cdot}5^\circ \quad c = 3{\cdot}636,$
$(d.)\ [\alpha]_D = +102{\cdot}0^\circ \quad c = 2{\cdot}010,$
$(e.)$* $[\alpha]_D = +100{\cdot}0^\circ.$

(*a*) contained arabinon, (*b*) is pure arabinose, so are (*c*) and (*d*) practically, and (*e*) is contaminated with the products of the action of sulphuric acid on arabinose; it also contains a trace of galactose, yielding, on treatment with nitric acid, a trace of mucic acid; a trace of barium salt is also present; when we take that into account, and consider how the specific rotatory power is arrived at, we can easily see that the amount of matter of any kind, other than arabinose, is very small. The galactose and the more soluble gum acid, the barium salt of which is mentioned above as being precipitated with the barium sulphate and as being insoluble in strong alcohol on treatment of the syrup, are products of the further degradation of a small portion of the resting-stage acid.

If we now compare the numbers obtained for the optical activity of this acid and for the percentage of baryta in the barium salt with the same numbers obtained for either geddinosic acid or trigalactangeddic acid, we shall find that, although the sp. rot. power does not differ very much from that of the latter, being on the whole somewhat less, the percentage of baryta in the barium salt is materially less than that in barium trigalactangeddate, or in barium geddinosate, in other words, the resting-stage acid of the acids of the B sample is of greater molecular weight than that of the A sample of acids. The question which then presented itself is, to what is this due? Is it that the resting stage of the B sample contains more galactan groups, or is it that the substances are altogether differently constituted? If the former supposition be correct, the resting-stage acid of the B sample when acted upon by sulphuric acid should yield final acids identical with those obtained from the A sample.

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* In this case the solid matter in solution was inferred from the sp. gr.; in all the other cases the crystals were dried at 100° and weighed; they contained no water of crystallisation.

A portion of the resting-stage acid, $[\alpha]_D = +20°$, and 7·2 per cent. baryta in the barium salt, was acted upon at the boiling temperature with 2 per cent. sulphuric acid solution for 1½ hours. The resulting liquid was cooled, neutralised with baryta-water, filtered, and concentrated in a vacuum. The syrup was repeatedly extracted with alcohol, the alcoholic solutions concentrated, and the residue allowed to crystallise. A determination of the optical activity of the crystals gave

$$[\alpha]_D = +81·0°.$$

On treatment with nitric acid, they yielded mucic acid. From these facts, and its solubility, crystalline habit, &c., the sugar is undoubtedly galactose. The solid matter in the mother liquid gave an optical activity

$$[\alpha]_D = +71·1°,$$

but it contained a little barium salt, hence it is clear, the alcoholic solution contained no other sugar except galactose, the coloured substances produced by the action of the acid on galactose, and a little barium salt of a gum acid, to be described later on.

The transformed products insoluble in alcohol, that is, the gum acids, were completely freed from sulphuric acid and sugar by treatment with alcohol, and then divided into two fractions, R_1 and R_2, and barium salts of them prepared.

0·653 gram R_1-salt, in dry state, gave 0·137 gram $BaSO_4$.
0·700 ,, R_2-salt ,, ,, 0·146 ,,
2·614 ,, R_1-salt ,, ,, 100 c.c. solution, sp. gr. 1·01316, and this, in a 200-mm. tube, gave a rotation $\alpha_D = +2·72°$.
2·800 grams R_2-salt gave 100 c.c. solution, sp. gr. 1·01412, and this, in a 200-mm. tube, gave a rotation $\alpha_D = +2·85°$.

Barium salt of R_1 = 13·8 per cent. BaO; D = 5·04,
,, R_2 = 13·7 ,, ,, ; D = 5·04.
Free acid, R_1. $[\alpha]_D = +60·2°$,
,, R_2. $[\alpha]_D = +58·8°$.

There is no doubt we have here a fairly pure substance; it is, in fact, monogalactangeddic acid—compare optical activity and percentage of baryta in the barium salt.

The more soluble portion of the gum acids obtained in the above degradations of the resting-stage acid was purified as usual and divided into two parts, G_1 and G_2, and of these baryta salts were prepared.

0·255 gram G_1 salt, dry, gave 0·051 gram $BaCO_3$.
0·771 „ G_2 „ 0·173 „ $BaSO_4$.
5·436 grams G_1 „ 100 c.c. solution, which, in a 200-mm. tube, gave a rotation $[\alpha]_D = +6·25°$.
3·856 grams G_2 salt, dry, gave 100 c.c. solution, which, in a 200-mm. tube, gave a rotation $\alpha_D = +4·25°$.

Barium salt, G_1 = 15·5 per cent. BaO,
„ G_2 = 14·7 „ „
Free acid, G_1. $[\alpha]_D = +67·6°$,
„ G_2. $[\alpha]_D = +64·7°$.

0 2817 gram G_1 dry free acid gave H_2O 0·149 gram, CO_2 0·440 gram.

	Found.	β-Geddinosic acid.		Theory for $C_{29}H_{48}O_{27}$.
C	42·60	42·48	42·54	42·03
H	5·88	5·89	5·93	5·77
				$C_{29}H_{48}O_{27}$-BaO.
BaO......	15·5	15·7	15·7	15·6

A comparison of these numbers with those obtained for β-geddinosic acid shows clearly that the acids are identical; hence β-geddinosic acid is the product of the degradation of the gum acids of both gums.

Further, when this acid was digested for an hour longer with sulphuric acid, an acid was obtained containing increased percentage of BaO, and I have no doubt, if the digestion be continued sufficiently long, an acid can be obtained the optical activity of which is

$$[\alpha]_D = +71°,$$

and the barium salt of which contains 18·76 per cent. BaO, hence geddic acid, $C_{23}H_{38}O_{22}$.

Let us now inquire what relationship does the resting-stage acid hold to this one;

$$C_{23}H_{38}O_{22} + 4C_{12}H_{20}O_{10} - 4H_2O = 4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18}$$

represents *tetragalactangeddic* acid.

An elementary analysis of the barium salt of the resting-stage acid yielded the following results:—

0·3125 gram dry barium salt of purified resting-stage acid gave H_2O 0·157 gram, CO_2 0·471 gram, $BaCO_3$ 0·0299 gram.

	Found.	Calculated for $4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18},BaO$.
C	41·72	41·7
H	5·58	5·4
BaO	7·43	7·49

Hence, the resting-stage acid for the gum acids of the B sample of gum is tetragalactangeddic acid, in the place of trigalactangeddic acid for the A sample.

I have shown that arabinon and arabinose and tetragalactangeddic acid were the only products of the action of sulphuric acid on the original gum acid. Let us see what is the composition of these acids. The molecular weight of the acid $[\alpha]_D = +90°$, with calcium salt containing 1·7 per cent. CaO, is 5600 ÷ 1·7 − 56 = 3238, and the molecular weight of tetragalactangeddic acid is 1890; hence the molecular weight of the matter eliminated is 3238 − 1890 = 1348. The molecular weight of arabinan is 264; hence 1348 ÷ 264 = 5·1, say 5, the number of molecules of arabinan hydrated. The acid under consideration is, therefore, *pentarabinantetragalactangeddic acid*,

$$5C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18}.$$

Several combustions of the free acid and of the calcium salt were made, different preparations being employed.

I. 0·2987 gram dry, free acid, gave H_2O = 0·167 gram, CO_2 = 0·488 gram; ash, a trace.

II. 0·3568 gram dry, free acid, gave H_2O = 0 200 gram, CO_2 = 0·587 gram; ash, a trace.

III. 0·3640 gram dry, free acid, gave H_2O = 0·207 gram, CO_2 = 0·602 gram; ash, a trace.

IV. 0·3628 gram dry calcium salt gave H_2O = 0·194 gram, CO_2 = 0·585* gram, and $CaCO_3$ = 0 0099 gram.

V. 0·2685 gram dry calcium salt gave H_2O = 0·145 gram, CO_2 = 0·436* gram, and $CaCO_3$ = 0·0086 gram.

VI. 0·2946 gram dry calcium salt gave H_2O = 0·163 gram, CO_2 = 0·476* gram, and $CaCO_3$ = 0 0099 gram.

	Found.						Theory for $5C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18}$.
	I.	II.	III.	IV.	V.	VI.	
C....	44·65	44·87	45·10	44·65†	45·09†	44·90†	45·23
H....	6·22	6·23	6·32	6·03†	6·11†	6·26†	5·92
							$5C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18},CaO$.
CaO..	—	—	—	1·52	1·7	1·8	1·71

* This includes the CO_2 in the ash in boat, determined by weight of boat before treatment with ammonium carbonate.

† These percentages are calculated on the substance free from ash.

These figures leave no doubt that the theory advanced for the constitution of the gum acid is the correct one.

The acid of the B fraction, $[\alpha]_D = +100—101°$, gave a calcium salt containing 1·4 per cent. lime; *heptarabinantetragalactangeddate* of calcium $7C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18},CaO$, requires 1·48 per cent. CaO.

Of this acid and its calcium salt several combustions were made, different preparations being employed.

I. 0·2907 gram dry free acid gave H_2O = 0·163 gram, CO_2 = 0·480 gram, and a trace of ash.

II. 0·2873 gram dry free acid gave H_2O = 0·159 gram, CO_2 = 0·476 gram, and a trace of ash.

III. 0·2284 gram dry free acid gave H_2O = 0·128 gram, CO_2 = 0·380 gram, and a trace of ash.

IV. 0·2886 gram dry calcium salt gave H_2O = 0·158 gram, CO_2 = 0·474 gram, and $CaCO_3$ = 0·0075 gram.

V. 0·2096 gram dry calcium salt gave H_2O = 0·115 gram, CO_2 = 0·346 gram, and $CaCO_3$ = 0·0050 gram.

	Found.					Theory for
	I.	II.	III.	IV.	V.	$7C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18}$.
C....	45·03	45·19	45·37	45·45*	45·63*	45·26
H ...	6·23	6·15	6·23	6·17*	6·18*	5·94
						$7C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18}CaO$.
CaO .	—	—	—	1·48	1·34	1·48

The highest rotating acid, $[\alpha]_D = +108—110°$, gave a calcium salt, which yielded CaO = 1·1 and 1·3 per cent.; calcium *nonarabinantetragalactangeddate*, $9C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18},CaO$, requires CaO = 1·29 per cent.

No serious attempt was made to purify the low rotating acid; it was exceedingly difficult to free any portion of it from nitrogen, but it was found that the fraction with optical activity $[\alpha]_D = +80—83°$ yielded a lime salt containing CaO = 1·9—2·0 per cent.; calcium *triarabinantetragalactangeddate*, $3C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18},CaO$, requires CaO = 1·98 per cent.

It is, therefore, satisfactorily proved that the portion of the gum free from nitrogen consists of the calcium, magnesium, and potassium salts of four acids, viz.:—

1. Nonarabinantetragalactangeddic acid, $9C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18}$.
2. Heptarabinantetragalactangeddic acid, $7C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18}$.
3. Pentarabinantetragalactangeddic acid, $5C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18}$.
4. Triarabinantetragalactangeddic acid, $3C_{10}H_{16}O_8,4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18}$.

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* Calculated on substance free from ash.

The heptarabinan acid exists in by far the largest quantity.

In purifying these acids, there was some evidence, as I have said, of the presence of intermediate acids; I have, however, satisfied myself that such substances do not exist in any quantity in the gum under examination. There are, no doubt, places for them, as there would appear to be no reason why we should not have *octa-*, *hexa-*, and *tetra-*arabinan acids; it is curious, indeed, that only the odd number arabinan acids come to the surface, so to say, in this gum.

A comparison of the composition of the series of acids in the two samples of gum shows clearly the difference between them, and the close relation they bear one to the other; I need not dwell further on the subject.

Besides the acids above described, the B sample of gum contains, as I have already said, a large quantity of substance which I found it impossible to free from nitrogen. I must reserve for a future occasion a fuller account of this sustance; its general characteristics are given above. The low percentage of ash in the B samples of gum is no doubt in part due to the presence of this substance, but the chief cause of it is the greater molecular weight, and consequently lower neutralising power, of the acids of this gum.

Although the evidence adduced for the conclusions arrived at in this work leaves little to be desired, I could not help feeling, notwithstanding many repetitions and confirmations, that there were a few points I should like to see more completely worked out. I could not do this in consequence of the difficulty in working with the B sample, due to the presence of the nitrogenous substance and to the high solubility of the gum acids in alcohol. I tried several other samples of commercial gedda gum, but could not find any one so easily workable as the A sample, the great bulk of which I had unfortunately used up. I have, therefore, to content myself with leaving the work as it is, for the present. In time, I hope to be able to describe more fully and accurately the different acids, and more especially to give a complete account of the final acid, *geddic acid*, $C_{23}H_{38}O_{22}$, $[\alpha]_D = +71—72°$, and to determine in what it agrees with and differs from the similar and isomeric acid of the arabin series. This acid we should now call *arabic acid*, the *resting-stage* acid in the arabin series being *tetragalactanarabic acid* (Trans., 1884, **45**, 55), the acid of the barium salt of which yielded 7·36 per cent. BaO the result of the action of sulphuric acid for 15 minutes on arabin: $4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18},BaO$ requires 7·49 per cent. BaO. This formula is $C_{71}H_{110}O_{58}$, against $C_{71}H_{112}O_{59}$, or a molecule of water less than that given in the place quoted. Arabin, or the then arabic acid, would be *diarabinantetragalactanarabic* acid $2C_{10}H_{14}O_{8},4C_{12}H_{20}O_{10},C_{23}H_{30}O_{18} = C_{91}H_{142}O_{74}$, against $C_{89}H_{142}O_{74}$, given, in the paper quoted. In the third part of this work, I shall, I hope, be able to make these points clearer.

Finally, I cannot conclude this paper without a brief account of the results obtained in an examination of a third sample of gedda gum.

Sample of Gedda Gum C.

This sample contained less nitrogenous matter than the B sample, but considerably more than the A one. The free acids were still more soluble in alcohol than those of the B sample; they had, however, the same syrupy character when precipitated by alcohol. In consequence of the high solubility of the gum acids in alcohol, I found it impossible to effect a clean fractionation. Sufficient, however, was done to show that the sample consisted of mixed gums, that, in fact, it contained at least two series of acids, neither of which was the same as the acids of the series of either the A or B samples.

The nitrogenous matter was again the portion least soluble in alcohol, but it was exceedingly difficult to free the gum acids from it. The portion rendered as free as possible from it was divided into *a*, *b*, and *c* fractions, *a* being the least soluble, and these, after being dialysed, were again divided into a_1 and a_2; b_1, b_2, b_3, b_4; and c_1, c_2, c_3, and c_4. The barium salts of these fractions were prepared and analysed. It would serve no useful purpose to give the analytical data. I may, however, record the results:—

a_1. $[\alpha]_D = +64{\cdot}9^\circ$; BaO = · per cent.
a_2. $[\alpha]_D = +77{\cdot}1^\circ$; BaO = · „
b_1. $[\alpha]_D = +83{\cdot}2^\circ$; BaO = 3·60 „
b_2. $[\alpha]_D = +82{\cdot}1^\circ$; BaO = 3·54 „
b_3. $[\alpha]_D = +83{\cdot}9^\circ$; BaO = 4·03 „
b_4. $[\alpha]_D = +84{\cdot}2^\circ$; BaO = 3·77 „
c_1. $[\alpha]_D = +85{\cdot}6^\circ$; BaO = 3·91 „
c_2. $[\alpha]_D = +88{\cdot}1^\circ$; BaO = 3·93 „
c_3. $[\alpha]_D = +89{\cdot}9^\circ$; BaO = 3·66 „
c_4. $[\alpha]_D = +92{\cdot}3^\circ$; BaO = 3·53 „

The fraction b_4 was acted upon with sulphuric acid for 30 minutes. The sugars formed consisted chiefly of arabinose with a little arabinon, and only a trace of galactose. In this case, the arabinose crystallised from the concentrated alcoholic solution in beautiful, warty aggregations.* The gum acid insoluble in alcohol was freed from sugar and sulphuric acid in the usual way and then divided into three fractions, *x*, *y*, *z*. Of these, barium salts were prepared and analysed:—

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* I may here remark that the crystalline habit of arabinose varies with the source whence it is obtained.

x $[\alpha]_D = +32{\cdot}2°$; BaO = 6·80 per cent.
y. $[\alpha]_D = +30{\cdot}0°$; BaO = 6·77 „
z. $[\alpha]_D = +31{\cdot}4°$; BaO = 6·84 „

Barium pentagalactangeddate, $5C_{12}H_{20}O_{10},C_{23}H_{28}O_{17},BaO$, requires 6·51 per cent. BaO. The fractions b_4 to c_4 are, no doubt, members of the same series. c_4 is probably *heptarabinanpentagalactangeddic acid*, $7C_{10}H_{16}O_8,5C_{12}H_{20}O_{10},C_{23}H_{28}O_{17},BaO$, requires 3·64 per cent. BaO, and c_1, *hexarabinananpentagalactangeddic acid*,

$$6C_{10}H_{16}O_8,5C_{12}H_{20}O_{10},C_{23}H_{28}O_{17},BaO,$$

requires 3·88 per cent. BaO, the intermediate substances being mixtures of these two acids.

a_1 does not belong to this series, for although it is the least soluble and its optical activity is lowest, the percentage of barium in the barium salt excludes it from the group; it evidently belongs to a distinct gum, the sample being, no doubt, a mixed one. a_2, b_1, b_2, and b_3 are obviously mixtures of this series and the pentagalactan series.

The nitrogenous substance in the C sample behaves in the same way to reagents as that of the B sample; it is, however, devoid of diastatic action.

Although the work described in this paper shows clearly the constitution of these dextrorotatory gums, and, indeed, of the whole group of gums, in a broad way, there are many points of interest which I should like to see more definitely settled. For example, the acids of the A sample differ one from the other by a molecule of arabinan; there is a difference in specific rotatory power between the mon- and di-acids of 6°, and between the di- and tri-acids of the same amount, whilst the difference between the tri- and tetra-acids appears to be 10°; it would be interesting to have these differences accurately determined, and to ascertain if they are constant factors. Of course, the amount of time requisite to purify the number of substances with which I had to deal, and to make accurate determinations of them was far greater than I could devote to the work. I had, therefore, to be satisfied with such factors as enabled me to identify the compounds and to decide that they were sufficiently pure to warrant the inferences drawn from the analyses of them. Again, we see the four acids of the B sample, which differ one from the other by two arabinan molecules, differ in specific rotatory power by about 10°, but when the final three arabinan molecules are eliminated, that is, when triarabinantetragalactangeddic acid is converted into tetragalactangeddic acid, there is a fall of 50°; the elimination of the one final molecule of arabinan in the A sample acids, the degradation of monarabinantrigalactangeddic acid to trigalactangeddic acid is accompanied by a fall of 15—18°. In the acids of the C sample of gum the difference of one molecule of arabinan makes, as in the A sample series, apparently a difference of 6—7° in the specific rotatory power of the acids, and the elimination of the six final molecules makes a difference of 50°, or about 8° for every molecule of arabinan.

Yet again, turning to the elimination of the galactan groups; between trigalactangeddic acid and the tetragalactan one there appears to be a difference in optical activity of only 2°. I believe, however, this might very well be increased to 7° in consequence of the nature of the impurities with which the preparations of both acids are likely to be contaminated. The specific rotatory power of digalactangeddic acid I believe to be about $[\alpha]_D = +11°$, thus differing from the trigalactan body by 7—8°; but there can be no doubt the mon-acid is close upon $[\alpha]_D = 60°$, whereas the difference between this and the final acid is not more than 11°. We see that with the elimination of the galactan groups the optical activity goes rapidly up after we pass the di-acid; the presence of a small quantity of the low acids in the preparation of the di- and tri-acids would materially increase their optical activity (compare some of the fractionations of the tri-acid, A sample). It is pretty clear, in a broad way, that the optical activities and the composition are closely related; I should like to be able to indicate the relationship more closely than is shown above. This could only be done by very careful purification of the substances and accurate determinations of the factors: it is obvious these things are beyond the scope of this paper. I hope, however, to be able to return to them later on, but, after all, the questions are more interesting from a physical point of view than a chemical one

There is one point more to which I should like to refer, the baryta in the barium salts; when the acids are dry, water appears not to take the place of baryta, the dry acids are anhydrides. This, I say, appears to be the case, as a result of a general analysis, but it would be well to have special evidence on the subject. This, I believe, I shall be able to obtain by employing more easily workable gums. In the immediate future, however, I intend to continue this work with an investigation into the constitution of an optically inactive gum, of which I have an example in a sample of Australian gum, and to conclude it with a full examination of the final acids, geddic acid, arabic acid, &c, $C_{23}H_{38}O_{22}$, in all cases.

Finally, I need hardly say that the amount of labour involved in this work, especially when it is remembered that what I have recorded here is only a fraction of the work upon which the results are based and which led to them, could not be performed without much assistance. For that assistance, given in a helpful and thoughtful manner, I have to express my best thanks to my assistant, Mr. A. L. Stern, B.Sc.

XCII.—*Dissociation of Liquid Nitrogen Peroxide.*

By J. Tudor Cundall, B.Sc., Lecturer on Chemistry in the Edinburgh Academy.

Whilst examining nitrogen trioxide with Professor W. Ramsay (Trans., 1885, **47**, 187 and 672), we were led to expect from the appearance of the substance that it was to a certain extent dissociated while yet in the liquid state. It was suggested that I should make some colorimetric experiments to ascertain whether this was the case, commencing with nitrogen peroxide as a substance for which experimental methods might be more easily devised than for the trioxide.

It was assumed that liquid nitrogen peroxide at low temperatures was a colourless substance, consisting of nitrogen tetroxide, N_2O_4, but as the temperature was raised it became yellow and then red, owing to its partial dissociation into NO_2. $N_2O_4 = 2NO_2$; NO_2 being assumed to be an intensely red substance, resembling bromine in appearance. Judging, too, from the behaviour of the substance in the gaseous state, where the change of colour is accompanied by decrease in the density, these assumptions seem not unreasonable.

At the time, I made some experiments in which chloroform solutions of the peroxide were matched against different coloured liquids. However, although the results seemed promising, the difficulties of obtaining a good match for the peroxide, and of keeping its solution, during the experiment, without loss of strength, and from the action of atmospheric moisture, proved insuperable with the crude apparatus I had then devised. The pressure of other work prevented any development of the idea until 1889, when the present research was commenced.

The object in view was, firstly, to decide whether liquid nitrogen peroxide dissociates when it is diluted; and, secondly, to measure its dissociation when heated. With regard to the first point, Ramsay has shown (Trans., 1888, **53**, 621), from the depression of the freezing point of acetic acid by varying amounts of peroxide, that no large amount of dissociation takes place on dilution. That alteration of temperature produces dissociation, as indicated by the colour, is obvious: and it has been shown by J. J. Boguski (*Compt. rend.*, **109**, 804—806), that the electrical resistance of slightly impure peroxide rises with the temperature.

Preparation of the Materials.

Ramsay (Trans., 1890, 57. 590) suggests that the best method of preparing nitrogen peroxide is to act on arsenic trioxide with nitric acid, and so obtain a mixture of trioxide and peroxide. This mixture is purified by oxidising the trioxide to peroxide, by treatment with nitrogen pentoxide, and subsequent distillation. He deprecates the use of sulphuric acid to prevent the formation of the trioxide on account of the diminished yield, but that objection can be obviated to a large extent by the use of fuming nitric acid, so that the amount of sulphuric acid required is kept low.

The plan I have found most effective is to mix 315 grams of fuming nitric acid (sp. gr. 1·5) with 150 grams of concentrated sulphuric acid and 250 grams of moderately finely powdered arsenic trioxide. The proportions are roughly those required for the reaction, $4HNO_3 + As_2O_3 = 2N_2O_4 + 2HAsO_3 + H_2O$. The arsenic trioxide is purposely in excess, and there is enough sulphuric acid to allow one formula-weight to each formula-weight of water present in the nitric acid formed in the reaction.

The mixture was made in a flask of about 1 litre capacity, fitted by a cork with an upright, thin-walled tube 1 cm. in diameter. This tube passed through the cork nearly to the bottom of the neck of the flask (an expedient which greatly protects the cork from the fumes), and projected about 30 cm. The projecting part was surrounded by a vessel of water, kept at 20—25°, to condense any nitric acid that might be carried over. The gas issuing from the top of the upright tube was then passed through a long U-tube containing phosphorus pentoxide, and finally into a bulb surrounded by ice and hydrochloric acid, where it was condensed. The action was started by gently heating the mixture; it then proceeded quietly, with occasional heating, until the mixture began to turn green, and the character of the effervescence to change, when it was stopped.

The crude product was then distilled at as low a temperature as possible. As it was feared that it might contain traces of anhydrous nitric acid, which is soluble in the peroxide, the vapour was passed through a tube of heated arsenic trioxide, and again through phosphorus pentoxide before being condensed as above. It was condensed in three fractions, the first weighing 97·5 grams, the second 56·0 grams, and the third 16 5 grams. The last fraction, as well as the residue in the flask, was not used. The portions collected are about 82 per cent. of the theoretical yield if the nitric acid of sp. gr. 1·5 contained 90 per cent. of HNO_3.

As in the subsequent experiments, it would be necessary to find the volume of small quantities of the peroxide accurately, and as the substance examined by Thorpe (Trans., 1880, **37**, 141) was prepared in quite another way, the sp. gr. and expansion were carefully determined by a method similar to that employed by Thorpe. A dilatometer, whose bulb held about 20 c.c., was used, and the following results were obtained (weight of peroxide taken 25·6225 grams) :—

t.	Sp. gr. compared with water at 4°.
0°	1·4880
6 7°	1·4734
11·8°	1·4649

Thorpe found the sp. gr. at 0° = 1·4903.

The chloroform used for dilution was that sold as "pure," and prepared by Messrs. Duncan and Flockhart from methylated spirit. It was dried with fused calcium chloride and distilled, the middle portion was then repeatedly treated with phosphorus pentoxide and distilled again, that portion only being employed which was of constant boiling point.

The solutions of nitrogen peroxide in chloroform were usually prepared by weighing in sealed bulbs, but were also prepared by measurement of the nitrogen peroxide in a special narrow graduated tube, and of the chloroform in a stoppered burette. The temperature was noted and correction made for it in calculating the strengths of the solutions, which are stated in percentages of nitrogen peroxide by volume at 0°. In almost all cases, the calculated strengths of the solutions were confirmed by analysis.

The method adopted was that of shaking in a small stoppered bottle a suitable volume of the solution with a measured quantity (usually 20 c.c.) of normal caustic soda, and titrating with semi-normal sulphuric acid, phenolphthaleïn being used as an indicator. This method was proved to give accurate results by check analyses in which weighed bulbs of the peroxide were broken in chloroform and then analysed. The method of analysis by the nitrometer was also employed with similar, but not as satisfactory, results.

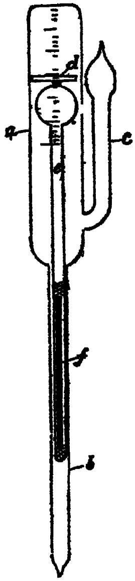
The solutions were prepared just before they were examined, except when they were sealed up in the colorimeter itself, and so unable to alter in strength.

Apparatus used.

It was obvious that some special form of colorimeter must be employed, in which to make the comparisons of tint, as the free access of air which obtains in the common forms was out of the question, and also the observations had to be made under known and steady conditions of temperature.

One of the most suitable forms devised was a modification of Mill's colorimeter. Of this pattern, two, called A and B, were constructed of different lengths for use with pale and darker solutions; they were alike in all other particulars. Each consisted of a tube, *a*, Fig. 1, about 22 mm. in diameter, in A 60 mm. long, and in B 100 mm. long, closed at the top by an end that was blown as flat and as thin as possible. At the other end, a narrow tube *b*, 7 mm. in diameter, and 200 mm. long, was sealed axially, and at the side a bent tube *c* with a small bulb was attached. Before the top of *a* was closed, the disc *d* and its float *e* was inserted. The disc was secured by a clip of platinum sealed to the top of the bulb and stalk of which the float consisted. The stalk was weighted with a piece of stout iron wire fixed inside with a plug of asbestos, so that the whole float and disc just floated in chloroform. The end of the stalk was then sealed. When the apparatus was constructed, *a* was graduated in mm., starting as nearly as possible from the inside of the flat end. It was filled with the required solution through the open end of *b*, and when nearly full was sealed. The bubble was then transferred to *c*, where it did not interfere, and also allowed the liquid to expand. The disc with its float was moved up and down, or fixed by the

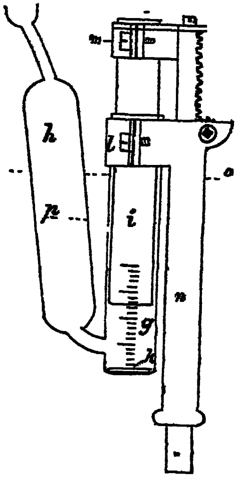
FIG. 1.



action of a small solenoïd encircling the jacketing tube in which *b* was supported. It was thus possible to make colour comparisons in an entirely-sealed apparatus.

For shorter columns, and for comparisons in which it was necessary to dilute during the progress of the experiment, two colorimeters of another form, called E and F, were employed. Each apparatus consisted of a straight tube *g*, Fig. 2, open at the top and closed at the bottom by a flat end, with a reservoir *h* sealed on near the bottom. A narrow inlet tube, provided with a slight funnel expansion, was sealed to the top of *h* for introducing the substance to be examined. In E, *g* was 100 mm. long; in F, 120 mm. long; and in both 22 mm. wide. Closely fitting into *g* was a tube *i* closed at the bottom with a flat end. In order to make the end of *i* of uniform thickness, it was ground and polished on the outside, whilst a microscope cover-glass was cemented on the inside with Canada balsam. This device provided a transparent end to the tube, which did not distort the disc *k* lying on the bottom of *g* when seen through it, and, above all, was not affected by the liquid in which it was immersed. The tube *g* was graduated

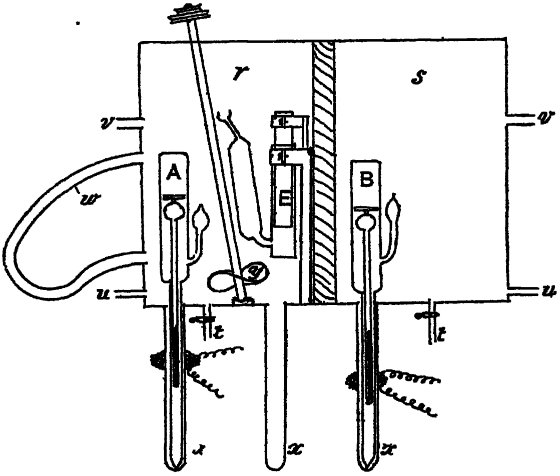
FIG. 2.



in mm., and as the levels of the top of the disc and of the bottom of the tube *i* could be accurately read, the length of the column between them could be determined with a limit of error of 0·2 mm. The tops of *g* and *i* were held in brass clamps *l* and *m*, which could be separated and approached by a rack and pinion working in a brass pillar *n*. This pillar fitted in a socket on the bottom of the constant temperature-bath, of which the level of the water rose to about *o*, whilst the level of the liquid in the colorimeter was never higher than *p*. The rack and pinion was actuated from the outside by a key, which passed through the wall of the bath. The only access of air was through the inlet tube and the narrow annular space between *g* and *i*. The effect of any deterioration through these openings was so minimised by the large bulk of liquid in *h* as to be negligible.

In order to obtain the necessary conditions of temperature and illumination, the colorimeters were enclosed in a wooden tank, Fig. 3, 26 cm. long by 13 cm. wide by 23 cm. deep, provided with a double glass front. The tank was divided into two equal parts, *r* and *s*, by a thick, watertight, wooden partition, and the whole was painted black. Both compartments were provided with drain cocks *t*, *t*, and with over-pipes *v v*. A supply of water could be allowed to flow in from the main by taps *u*, *u*. In the side *r* was fixed a metal pipe *w*, which, when heated at its upper part, caused a circulation of hot water, and permitted the temperature of the bath to be raised. Tubes *x*, *x*, *x*, on which the solenïds slid stiffly, were provided in both compartments as sockets for the colorimeters A and B, whilst a socket for the reception of the stand of colorimeters E and F was fixed in *r*. Uniformity of temperature was secured by an Archimedean screw *y*, fixed at an angle and turned rapidly by an electromotor. This stirred so effectively that when ice and water were in the bath, the temperature remained absolutely constant in every part until almost the last trace

FIG. 3.



of ice was melted. A similar stirrer was provided in the other compartment, but it was not much used as the temperature generally required there was that of the tap water, which was allowed to flow sufficiently rapidly to keep up a good circulation, and whose temperature remained constant during long periods. Higher temperatures in *r* were produced by regulating the size of the flame under *w*, and these, owing to the large mass of water and constant stirring, were easily kept uniform.

The measuring apparatus employed was checked either by weighing with water or against measures of known accuracy.

Method of Comparison and Calculation.

An attempt was made in the earlier experiments to compare the colour of the peroxide with the solution of some colouring matter such as chromic acid or Bismarck brown. As this plan proved unsatisfactory, it was given up in favour of a method in which different lengths of some standard solution of the peroxide were compared with the solution that was being diluted or raised in temperature. The method of procedure, initially, was to take some pure peroxide in colorimeter E at 0° and to compare it with a standard solution in colorimeter A or B either at the same or another temperature. The comparison was effected by fixing the disc in A or B and then matching the colour of that particular column of solution by moving the inner tube *i* of E or F up or down by the rack and pinion to increase or diminish the colour. In order to make the operation easier, the columns to be compared were put close side by side, and the whole of the bath and apparatus was shut off from view by a screen of card with two holes directly over the columns to be matched. The discs were illuminated by two gas jets so placed as to equally light them, and whose heat rays were cut off from the bath by a double screen of glass. The flames themselves were hidden from the eye by shades. When the colours in the two colorimeters were matched, the heights of the columns of equal tint were read and recorded. The solenoid was then moved and a new match made, and so on until five or more comparisons had been taken, when the liquid in E was diluted or its temperature raised, and a new match made. Great care was taken that the colorimeters and their contents were at the temperature of the bath by waiting a sufficient time and by stirring the liquids in them by the movement of the disc or tube.

Examples taken at random of these comparisons are given in order to show the amount of accuracy possible. It will be seen in the sequel that the errors that do occur—and shades of yellow and orange are notoriously difficult to match—are of a magnitude which do not affect the general result. A column of the peroxide 10 mm. in length at 0° was taken to be of unit depth of colour, and all the lengths given are those of columns matching it.

Pure peroxide at 0° was in E, and a standard solution called A/3 of 8·9 per cent. by volume was in A also at 0°.

E.		A.
3·6 mm.	match	22 mm.
5·8 „	„	32 „
3·0 „	„	18 „
5·9 „	„	32 „
2·0 „	„	12 „
20·3		116

Hence, at 0°, 57·1 mm. of the solution A/3 match 10 mm. of pure peroxide.

Again a solution of 3·0 per cent. at 0° in F was compared with a standard called B/3 of 1·44 per cent. by volume at 13·2° in B.

F.		B.
22·0 mm.	match	14·8 mm.
38·0 „	„	23·2 „
25·0 „	„	15·0 „
25·0 „	„	14·0 „
28·4 „	„	19·3 „
138·4		86·3

Now 63·9 mm. of B/3 at 13·2° had been found to match 10 mm. of pure peroxide at 0°, so at 0°, $\frac{63{\cdot}9 \times 138{\cdot}4}{86{\cdot}3} = 102{\cdot}5$ mm. of a 3 per cent. solution have the same tint as 10 mm. of pure peroxide.

The first column in Table I (p. 1084) gives the length of different solutions at 0° which have the same colour as 10 mm. of pure peroxide. The corresponding number in the second column is the percentage strength of the solution.

Now, if the colouring matter in the pure peroxide remains unchanged in amount by dilution, then the product of the length of the columns that match into their strengths should be constant, for the lengths should vary inversely as the percentage strength by volume, that is, if you halve the strength of a solution it ought to require a column of double length to give the same colour. The third column gives the product of length by strength, and it is seen that it is not a constant, but diminishes with increased dilution. The colouring matter then increases with the dilution, and its relative quantity is as the reciprocal of the product length by strength, for example, if at 0° a 10-mm. column of pure peroxide (100 per cent.) matches a 40·6 mm. column of 10·1 per cent., then we have a column containing 100 × 10 = 1000 parts of peroxide matching a column containing 40·6 × 10·1 = 410 parts. Therefore the relative amounts of colouring matter (NO_2) in the 10·1 per cent. solution to that in the pure peroxide are as $\frac{1}{410} : \frac{1}{1000}$, or as 2·44 : 1. This reciprocal multiplied by 1000, which expresses the relative amount of NO_2 present, is stated in the fourth column. It is multiplied by 1000, so that the amount present in the pure peroxide at 0° is represented by one unit.

TABLE I.—*Comparison at 0° of the Colour of Pure Nitrogen Peroxide with that of its Solutions.*

Columns of equal tint.	Per cent. strength by volume.	Per cent. strength × length.	Relative amount of NO_2 present.
mm.			
10·0	100·0	1000	1 00
11·0	88·3	971	1·03
12·5	75·4	942	1·06
12·7	67·6	860	1·16
13·7	63·0	865	1 20
13·7	62·6	858	1·17
15·0	55·0	825	1·21
15·8	48·2	761	1·31
15·2	46·8	711	1·41
18·0	37·5	675	1·48
21·0	25·8	541	1·85
25·0	25·1	627	1 59
34·6	14·3	495	2 02
39·2	13·0	510	1 97
37·3	10·4	388	2·60
37·3	10·37	387	2·58
40·6	10·1	410	2 44
57·3	8·9	510	1·95
56·0	7 6	426	2·35
50·5	7·5	379	2·64
63·1	7·1	406	2·46
63·1	5·3	334	2 99
80·7	4·0	323	3·1
102·5	3·0	307	3·25
136·0	1·44	196	5·1
118·8	1·44	171	5 85

The last column is plotted as Curve I (p. 1086) against percentage strength by volume. It will be seen that the rate of dissociation is extremely small, until the peroxide is about 20 times diluted, after which it becomes much greater. It should be noted that these figures are purely relative, their absolute value being found later.

Measurement of Relative Dissociation on Rise of Temperature.

Having thus established that dilution produces dissociation, it became necessary to compare this dissociation with that caused by rise of temperature.

The comparisons were made, and the results calculated in precisely the same way as before; a 10 mm. length of pure peroxide at 0° being again taken as containing unit quantity of peroxide. The relative dissociation is plotted against temperature for eight different dilutions, as Curves VIII—XIV, in Plate II (p. 1086); the amount at 0° being corrected by reference to the smoothed curve representing the dilution at 0°.

TABLE II.—*Dissociation caused by Rise of Temperature at Different Dilutions.*

Columns of equal tint.	Temperature.	Per cent. strength by volume.	Per cent. strength × length.	Relative amount of NO_2 present.
mm.	°			
10·0	0·0	100·0	1000	1·00
5·4	7·2	100·0	540	1·85
4·1	11·2	100·0	410	2·40
15·2	0·0	46·8	711	1·41
11·1	4·2	46·8	519	1·92
7·0	9·2	46·8	328	3·05
5·3	15·2	46·8	248	4·03
21·0	0·0	25·8*	542	1·85
15·3	5·0	25·8	395	2·53
9·4	11·6	25·8	243	4·13
6·1	17·6	25·8	157	6·36
25·0	0·0	25·1*	628	1·59
14·6	7·2	25·1	366	2·73
6·5	17·3	25·1	158	6·15
34·6	0·0	14·3	495	2·02
26·0	5·7	14·3	372	2·69
18·0	10·7	14·3	257	3·87
12·5	15·7	14·3	179	5·59
8·1	20·2	14·3	116	8·66
37·4	0·0	10·1	378	2·64
30·1	5·4	10·1	304	3·29
21·3	11·2	10·1	215	4·67
14·4	15·7	10·1	145	6·89
11·0	20·2	10·1	111	9·06
6·96	27·0	10·1	70	14·2

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* These two percentages are combined in the same curve, No. X.

TABLE II—*continued.*

Columns of equal tint.	Temperature.	Per cent. strength by volume.	Per cent. strength × length.	Relative amount of NO_2 present.
mm.	°			
57·2	0·0	7·1	406	2·46
41·1	5·1	7·1	291	3·43
29·3	9·9	7·1	207	4·82
16·9	15·9	7·1	117	8·51
13·6	20·2	7·1	97	10·33
8·8	25·0	7·1	62	16·06
102·5	0·0	3·0	307	3·25
69·3	5·1	3·0	208	4 81
48·0	10 9	3·0	147	6·79
41 6	15 0	3·0	125	8·02
29·2	20·0	3·0	88	11·4
21·4	25·0	3 0	64	15·5
118·8	0 0	1·44	171	5·85
69·8	11 9	1·44	101	9·9
63·9	13·2	1·44	92	10·9
62·8	15·1	1·44	90	11·2
37·7	19·9	1·44	54	18 4
26·6	25·0	1·44	38	26·1

The amount of dissociation at every 5° for each of these strengths was then read off the smoothed rise of temperature curves, VIII—XV (Plate II), and plotted as dilution curves, II—VI (Plate I). These isothermals show that dissociation at temperatures above 0° takes place in the same manner as at 0°, only at a greater rate. The form of the curve below 10 per cent. is confirmed by a dilution experiment that was performed at 8·2°, and of which the results are stated in Table III. It is plotted as Curve VII (Plate I).

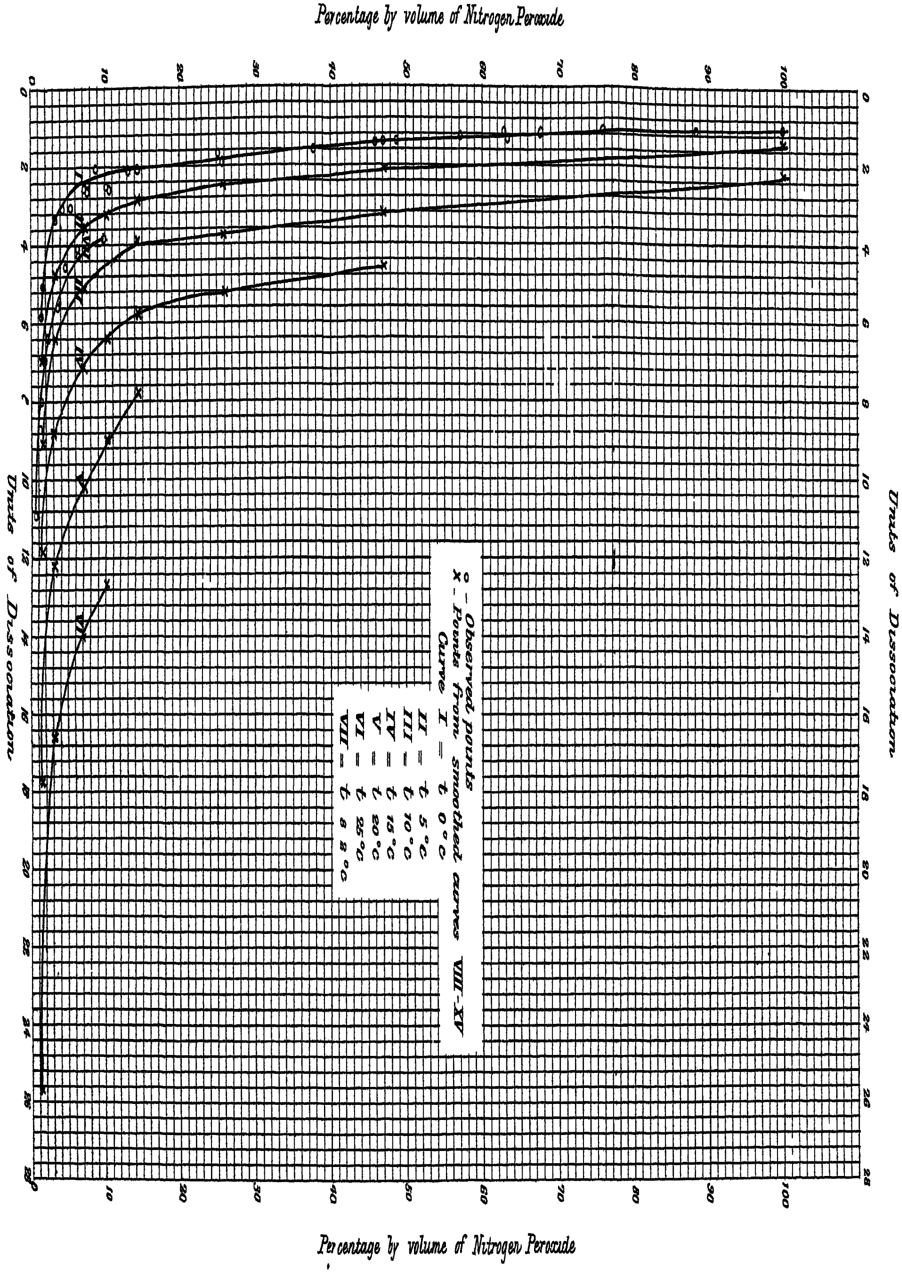
TABLE III.

Columns of equal tint.	Per cent. strength by volume.	Per cent. strength × length.	Relative amount of NO_2 present.
mm.			
26·5	9 93	263	3·8
37·6	6·0	226	4·4
45·8	4·8	220	4·5
48·8	3·6	176	5·7
61·5	2·5	154	6·5
71·6	2 0	143	7·0
77·5	1·6	124	8·06
82·1	1·4	115	8·7
111·5	0·8	89	11·2

"CUNDALL"

Plate I.

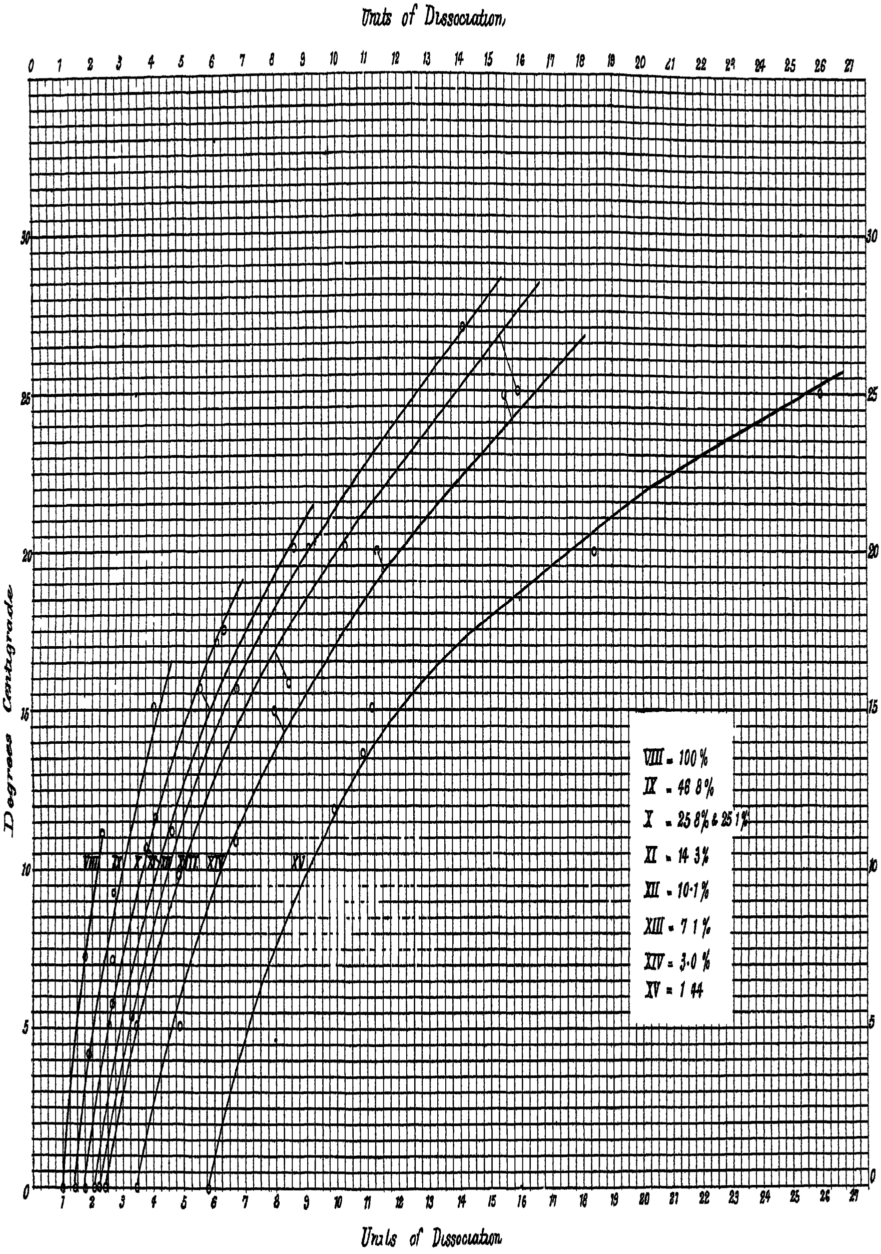
Journ Chem Soc Dec. 1891



CUNDALL

Plate II

Journ Chem Soc Dec 1891



HARRISON & SONS LITH S MARTINS LANE W C

Determination of the Absolute Amount of NO_2 *present.*

In order to arrive at the absolute amount of the peroxide dissociated, a comparison was made between the colour of the pure liquid peroxide at 0° with that of the gaseous peroxide at 30°. It is true that the substances compared are in different physical states, but it will be seen that the NO_2 present in the liquid peroxide and in the solutions is never in a state of aggregation differing widely from that obtaining in the gas, and so might be expected to have the same properties as regards colour as when actually in the gaseous state. That this assumption is legitimate is borne out by the fact that liquid and gaseous nitrogen peroxide have both the same absorption spectrum. that of the pure liquid being fainter than that of the gas; on dilution and rise of temperature, however, it becomes much more distinct. Again, another property of the molecule, namely, its action on polarised light, is the same in the liquid and gaseous state, provided equal numbers of molecules are traversed by the ray.

The comparison was made by means of a solution A/3 of 8·9 per cent. by volume, 22·5 mm. of which at 11·8° matched 10 mm. of the pure liquid peroxide at 0°. This solution A/3 in A was compared with the gas in F; F was filled with the gas by allowing about 1 c.c. of the liquid peroxide to run in at the inlet tube and cover the disc, where it soon evaporated, the excess escaping, and leaving the apparatus quite full of the gas. The temperature was allowed to become steady, and then matches were made in just the same way as with the liquid. After five matches had been made, a little more liquid peroxide was added, and when it had evaporated, and the temperature had become steady, comparisons were again made.

The results of the first series of comparisons are given in Table IV, where the gas in colorimeter F at 29·8° was compared with standard solution A/3 (of 8·9 per cent. by vol.) in colorimeter A at 12·0°.

TABLE IV.

A.		F.
30·8 mm.	match	12 mm.
19·5 „	„	7 „
11·0 „	„	5 „
21·0 „	„	9 „
13·0 „	„	6 „
95·3		39

Now, 22·5 mm. of A/3 at 12·0° matched 10 mm. of pure liquid peroxide at 0°, so at 29·8°, $\frac{39{\cdot}0 \times 22{\cdot}5}{95{\cdot}3} = 9{\cdot}2$ mm. of gaseous nitrogen peroxide have the same depth of colour as 10 mm. of liquid peroxide at 0°. The experiment was repeated on another day with gas from a different sample of peroxide, again comparing with standard solution A/3 at 11·8°. The temperature of the gas during the first five matches was 29·6°, but during the remaining 15 it only varied between 29·9° and 30°. The results are given in Table V.

TABLE V.

A.		F.
19·0 mm.	match	6·6 mm.
11·1 ,,	,,	4·0 ,,
20·0 ,,	,,	7·0 ,,
13·9 ,,	,,	5·0 ,,
21·5 ,,	,,	9·0 ,,
24·0 ,,	,,	9·9 ,,
16·6 ,,	,,	7·0 ,,
7·4 ,,	,,	3·0 ,,
12·5 ,,	,,	5·4 ,,
18·7 ,,	,,	8·0 ,,
16·0 ,,	,,	6·3 ,,
11·2 ,,	,,	4·9 ,,
16·2 ,,	,,	6·1 ,,
10·9 ,,	,,	5·1 ,,
18·1 ,,	,,	8·2 ,,
17·0 ,,	,,	7·0 ,,
11·6 ,,	,,	5·2 ,,
17·0 ,,	,,	8·1 ,,
8·4 ,,	,,	4·0 ,,
14·2 ,,	,,	7·0 ,,
305·3		126·8

Hence, calculating as before, 9·3 mm. of the gas at 30° match 10 mm. of the pure liquid peroxide at 0°. Now, by J. W. Gibbs' formula (*Amer. J. Sci.*, **18**, 1879), the density of nitrogen peroxide gas compared with air at 30° and 755·8 mm. (the pressure at which the matches were made) is 2·618, which agrees sufficiently well with Deville and Troost's experiments (*Compt. rend.*, **64**, 237) under similar conditions. Now, a density of 2·618 requires that the gas should contain 35·2 per cent. of NO_2 and 64·8 per cent. of N_2O_4. But there is the same amount of NO_2 in a column 9·3 mm. long of the gas at 30° and 755·8 mm. as there is in one of 10 mm. of pure liquid peroxide. Assuming that a column with a base of 1 sq. cm. is being looked at, 9·3 c.c. of the gas has as much NO_2 in it as 10 c.c. of pure peroxide at 0°. 9·3 c.c. at 30° and 755·8 mm. contain 35·2 per cent. of NO_2 = 3·78 c.c., which weigh $3{\cdot}78 \times \frac{273}{303} \times \frac{755{\cdot}8}{760} \times \frac{46}{22320}$ = 0·00698 gram of NO_2. Now, 10 c.c. of pure peroxide at 0° weigh 14·903 grams; therefore nitrogen peroxide at 0° contains $\frac{0{\cdot}00698}{14{\cdot}903} \times 100$ = 0·0468 per cent. by weight of NO_2.

The weight per cent. of NO_2 present in the peroxide in any of the solutions at any temperature examined can then be found by multiplying the number expressing the relative dissociation by 0·0468, as there is this amount in the pure peroxide at 0° which is taken as being dissociated to the extent of 1 unit.

Conclusions.

1. Liquid nitrogen peroxide dissociates when diluted with chloroform, just as the gas dissociates when diluted with an indifferent gas, or when the pressure on it is lowered. The dissociation is of small amount, and its rate of increase is very small until the liquid is diluted about twenty times, when it becomes much greater.

2. Liquid peroxide of nitrogen and its solutions dissociate when heated, but its solutions do so at a much greater rate as they are diluted. In the most dissociated solution yet examined, that is, one containing 1·44 per cent. by vol. of nitrogen peroxide at 25°, there is only 1·22 per cent. of NO_2 present in the peroxide

It is proposed to examine more dilute solutions at higher temperatures with a view to observing whether the liquid peroxide under those circumstances behaves like the gas, but as this will involve working at pressures greater than atmospheric, some considerable time must elapse before results can be obtained.

Edinburgh Academy.

XCIII.—*On Iron Carbonyls.*

By LUDWIG MOND, F.R.S., and CARL LANGER, Ph D.

THE existence of a volatile compound of iron and carbon monoxide was made known to the Society last session in a communication by one of us and Dr F. Quincke (Trans., 1891, 59, 604). In a paper read before Section B of the British Association in August last,* it was announced that we had succeeded in obtaining this compound in the form of an amber-coloured liquid, which boils at 102°, solidifies below —21°, and deposits tabular crystals of a darker colour on standing. We have since found that these crystals are only obtained when the liquid is exposed to light, and that their formation is accompanied by the evolution of carbon monoxide.

This liquid compound of iron with carbon monoxide is prepared in the following manner:—Ferrous oxalate, precipitated from a hot solution of ferrous sulphate by adding to it a slight excess of potassic oxalate, is washed by repeated decantation with water and dried at 120°. The dry powder is introduced into a combustion tube, and heated in a gentle current of hydrogen, the temperature being gradually raised until the oxalate has turned black, and is then kept stationary until, on arresting the current of hydrogen, no more gas escapes. The finely-divided iron thus obtained is allowed to cool to the ordinary temperature, and is then put into water without allowing it to come into contact with the air, boiled several times with water until all sulphate is removed, dried quickly on plates of gypsum, and then returned to the combustion tube and slowly heated in a current of hydrogen to about 300° to drive off all the water. After allowing it to cool again, the hydrogen is displaced by carbon monoxide and the tube is then closed at one end, the other remaining connected with the gasholder containing carbon monoxide, which is slowly absorbed by the iron. After the lapse of 24 hours, the tube is heated to about 120°, when the iron carbonyl formed distils over. The yield is somewhat increased when this distillation takes place in a slow current of carbon monoxide and the issuing gases are passed through a tube cooled to —20°. When no more iron carbonyl comes over, the tube is allowed to cool, and put into communication again with the gasholder containing the carbon monoxide, which is absorbed as before. This operation can be repeated during several weeks; the daily yield, however, is always small, and rarely exceeds 1 gram from

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* "On Nickel Carbon Oxide and its Application in Arts and Manufactures," by Ludwig Mond.

100 grams of iron. We have tried to increase this yield by exposing the iron to carbon monoxide under a pressure of 10 atmospheres, but have obtained no material augmentation.

The iron carbonyl thus obtained is a somewhat viscous liquid of a pale-yellow colour. Its sp. gr. at 18° is 1·4664 compared with water at 18°. It distils completely without decomposition at 102·8° under a pressure of 749 mm. It solidifies below —21° into a mass of yellowish, needle-shaped crystals. It is soluble in many organic liquids such as alcohol, ether, benzene, mineral oils, &c. On exposure to the air, it is slowly decomposed with formation of a brown precipitate consisting mainly of hydrated ferric oxide. On heating the vapour to 180°, the compound is completely decomposed into iron and carbon monoxide. The vapour density has been determined in a Victor Meyer apparatus filled with hydrogen and heated in a bath of xylene. We obtained the following figures :—

0·1912 gram substance displaced 25·0 c.c. hydrogen at 17·7°; air pressure, 751 mm.; density, 6·5.

0·1249 gram substance displaced 16·4 c.c. hydrogen at 17·7°; air pressure, 759 mm.; density, 6·4.

This corresponds very nearly to the calculated density of $Fe(CO)_5$ = 6·7, whilst $Fe(CO)_4$ would require 5·7, and $Fe(CO)_6$ 7·25. The formula $Fe(CO)_5$ is also corroborated by analysis of the substance.

We determined the iron by heating a weighed quantity with chlorine-water in a sealed tube and subsequently precipitating and weighing the ferric oxide; and the carbon monoxide by burning a weighed quantity in a current of air in a combustion tube partly filled with copper oxide, and weighing the carbon dioxide formed. The following figures were obtained :—

I. 0·3014 gram substance yielded 0·1265 gram Fe_2O_3 = 0·08855 gram Fe.

II. 0·1318 gram substance yielded 0·05523 gram Fe_2O_3 = 0·03867 gram Fe.

III. 0·2463 gram substance yielded 0·2702 gram CO_2 = 0·17195 gram CO.

IV. 0·2838 gram substance yielded 0·3172 gram CO_2 = 0·2022 gram CO.

	Found.				Theory.
	I.	II.	III.	IV.	$Fe(CO)_5$.
Fe	29·37	29·34	—	—	29·08
CO	—	—	69·88	71·14	70·92

We propose to call this compound ferropentacarbonyl. It is isomeric with ferrous croconate, C_5FeO_5.

Ferropentacarbonyl is not acted upon by dilute sulphuric, hydrochloric, or nitric acid at the ordinary temperature. Concentrated nitric acid, chlorine-water, and bromine-water, however, act readily, forming ferric nitrate, chloride, or bromide respectively.

Alcoholic solutions of sodium and potassium hydroxide absorb the vapour rapidly, and also dissolve the liquid without evolution of gas. After a while, a greenish precipitate is formed, which contains chiefly hydrated ferrous oxide, and the solution becomes brown. On exposing it to the air, it takes up oxygen, and the colour changes to a dark-red, whilst hydrated ferric oxide separates out. On account of this rapid change of the solution in contact with air, and the small quantity at our disposal, we have not yet been able to isolate any well-defined compound suitable for analysis from it.

On mixing alcoholic solutions of ferropentacarbonyl and mercury chloride, a slight evolution of carbon monoxide is observed, and a yellowish, crystalline precipitate is formed containing iron, mercury, chlorine, and carbon monoxide. The analyses, however, did not give figures from which a definite formula could be deduced The liquid ferropentacarbonyl undergoes no change when kept in the dark, but when it is exposed to the light for several hours in a sealed tube, gold-coloured, tabular crystals are formed, and the pressure in the tube rises very high. When dry, these crystals have a metallic lustre, and resemble flakes of gold. On exposure to the air, they are gradually decomposed and coloured brown. We have prepared this substance for analysis by collecting it on a filter, washing with ether, and drying over sulphuric acid for about 30 minutes. A weighed quantity was treated with bromine-water, which dissolves the substance with evolution of gas. The iron was precipitated from the solution and weighed as ferric oxide.

0·0800 gram substance yielded 0 0412 gram Fe_2O_3 = 0·02884 Fe, or 36·05 per cent. Fe.

0·0742 gram substance yielded 0·0381 gram Fe_2O_3 = 0 02662 Fe, or 35·90 per cent. Fe.

These figures agree sufficiently with the formula $Fe_2(CO)_7$ (diferroheptacarbonyl), which requires 36 36 Fe. We have, so far, not succeeded in obtaining a sufficient quantity of this substance to control its composition by determining the carbon monoxide, nor has it been possible to ascertain its molecular weight either by the vapour density or by Raoult's method, as the substance is neither volatile without decomposition nor sufficiently soluble in suitable solvents.

Chlorine, bromine, and nitric acid decompose the crystals; sulphuric acid and hydrochloric acid do not act upon them at the ordinary temperature. Alcoholic potash dissolves them, forming a solution similar in appearance and behaviour to that obtained with the liquid iron carbonyl.

The solution of iron carbonyl in heavy mineral oil investigated by Mond and Quincke, which gave figures for the proportion of iron to carbon monoxide varying from 1 : 4·03 to 1 : 4·26 undoubtedly contained mixtures of the two substances we have described.

We are continuing the investigation of these compounds, and hope shortly to make a further communication to the Society.

XCIV.—*Note on some Compounds of the Oxides of Silver and Lead.*

By Emily Aston, B.Sc. (Lond.), Chemical Department, University College, Gower Street.

According to Wohler (*Ann. Phys. Chem.*, 1837, **41**, 344) the yellow precipitate obtained by the addition of caustic potash to a solution of a lead and silver salt is a compound, containing 1 mol. of silver oxide to 2 mols. of lead oxide ($Ag_2O,2PbO$). It is insoluble in caustic potash, and so, by digestion with it, may be separated from the free lead oxide, which is simultaneously precipitated. On analysis, Wöhler obtained the numbers 34·23 per cent. Ag_2O and 65·77 per cent. PbO.

At Professor Ramsay's suggestion, I have made the following attempts to obtain Wohler's compound, but at present without success.

First Method of Preparation.—The first sample prepared was a yellow precipitate, obtained by the addition of a strong solution of caustic potash to a solution of lead acetate and silver nitrate, in which the ratio of lead oxide to silver oxide was approximately 3 : 1; the mean of two analyses gave 22·79 per cent. Ag_2O, and 77·18 per cent. PbO. The nearest formula is $7PbO,2Ag_2O$, which corresponds to 22·91 per cent. Ag_2O. This sample was then treated with a strong solution of caustic soda, and the residue, on analysis, yielded 48·19 per cent. Ag_2O, showing that a large amount of lead oxide had been dissolved. The formula PbO,Ag_2O corresponds to 50·98 per cent. Ag_2O.

A second yellow precipitate was obtained by the addition of potash to a solution of lead and silver nitrates, containing approximately 2PbO to $1Ag_2O$; the mean of two analyses gave 40·68 per cent. Ag_2O. This number approaches 40·94 per cent. Ag_2O, corresponding to the formula $3PbO,2Ag_2O$.

A third sample, somewhat darker in colour, was obtained by adding a very large excess of caustic potash to a solution of lead and silver nitrates containing approximately 1PbO to $1Ag_2O$; on analysis, it gave 49·01 per cent. Ag_2O as the mean of two estimations, a number not very far from that obtained with the first sample after extraction with soda (48·19 per cent.). This sample was extracted with ammonia to dissolve any free silver oxide (for it stained the skin), and then with soda. After extraction, it contained a still higher percentage of silver oxide, viz., 57·54.

Second Method of Preparation.—To ensure the presence of excess of caustic alkali, three more samples were prepared by the addition of silver nitrate to a solution of lead nitrate to which excess of pure caustic soda had been previously added; the colour of the precipitate obtained was yellow at first, but quickly turned to green in the case of samples 4 and 5; in the case of sample 6, it did not change from yellow to green for a few days. In common with other silver salts, the mixed lead and silver oxide is darkened by the action of light, so that the colour is apt to vary, unless the substance is kept in the dark.

The fourth sample was made by adding silver nitrate to lead nitrate in excess of soda, in such amount that the ratio of lead oxide to silver oxide was about 1·5 to 1; the precipitate obtained gave 56·81 per cent. Ag_2O.

The fifth sample was made by adding silver nitrate to lead nitrate in excess of soda, in such amount that the ratio of lead oxide to silver oxide was nearly 5 to 1; the precipitate, on analysis, gave 49·01 per cent. Ag_2O, a number agreeing with that obtained from sample 3 (49·01), and also very near sample 1, after extraction with soda (48·19).

The sixth sample was prepared with a still larger proportion of lead oxide, 9PbO to $1Ag_2O$; the precipitate obtained gave on analysis 47·46 per cent. of Ag_2O.

Third Method of Preparation.—A sample was then prepared according to Wöhler's method, by the addition of caustic soda to a solution of a lead and silver salt, and the precipitate repeatedly extracted with soda, till no more lead oxide was dissolved; the precipitate, which was originally yellow, turned first green and then black. On analysis, it yielded 66·29 per cent. Ag_2O; the nearest formula, $2Ag_2O,PbO$, corresponds to 67·53 per cent. Ag_2O.

Fourth Method of Preparation.—Another way was then tried. Lead hydrate and silver hydrate were mixed together, and allowed to stand for some weeks with a solution of soda; the mixture turned dark-green; it was then repeatedly extracted with soda till no more lead oxide was dissolved. On analysis, it gave 65·39 per cent. Ag_2O, a number not very far removed from that required by the formula $2Ag_2O,PbO$, viz., 67·53 per cent. Ag_2O.

Tabular Statement of Results.

Method of preparation.	Sample.	Found Ag_2O.	Ag_2O calculated for formula.	
		per cent.		
(i.) Mixture of lead and silver salts, precipitated by caustic potash...........	1	22·79	22·91	$7PbO,2Ag_2O$.
	2	40·68	40·94	$3PbO,2Ag_2O$.
	3	49·01	50·98	PbO,Ag_2O.
(ii.) Addition of silver nitrate to lead hydrate dissolved in excess of caustic soda....	4	56·81	50·98	PbO,Ag_2O.
	5	49·01		
	6	47·46		
(iii.) Method same as (i), but repeatedly extracted with soda..	7	66·29	67·53	$PbO,2Ag_2O$.
(iv.) From lead hydrate and silver hydrate by addition of soda solution.........	8	65·39	67·53	$PbO,2Ag_2O$.

These results seem to show:—

1. Under the conditions given by Wöhler, the substance formed varies in composition, the highest percentage of silver obtainable being 49·01, whereas the amount required for Wohler's compound is 34·23.

2. When a mixture of lead and silver hydrates is allowed to stand in presence of soda, a change of colour occurs, and after repeated extraction with soda, a substance is left having a composition nearly that required by the formula $2Ag_2O,PbO$. A compound of similar composition is obtained by precipitating the mixed nitrates of lead and silver, and exhaustively extracting with soda.

I also tried to obtain compounds of lead oxide with the oxides of barium, strontium, sodium, and potassium respectively, but without success. When a solution of a lead salt is added to a strong boiling solution of barium or strontium hydrate, crystalline scales of litharge of a yellowish-grey tinge are deposited on slight cooling. In the case of sodium and potassium hydrates, the solution had to be evaporated to a small bulk, and the crystals were not so well defined. Some attempts were made by evaporating a mixture of lead acetate and the hydrate over sulphuric acid, but without success; the result was in some cases a crystalline deposit of litharge, in others, crystals of the hydrate containing a little lead separated out, but of no definite composition.

University College, London.

XCV.—*A New Method of Preparing β-Dinaphthylene Oxide*, $C_{20}H_{12}O$, *and the Constitution of its Tetrasulphonic Acid.*

By W. R. Hodgkinson and L. Limpach.

This substance has already been prepared in a variety of ways: by heating naphthol with lead oxide (Graebe, Knecht, and Unzeitig, *Annalen*, **209**, 138), by long boiling of naphthol in contact with air (Merz and Weith, *Ber.*, **14**, 200), by heating naphthol with phosphoric anhydride, and by the dry distillation of calcium naphthylate (*Ber.*, **15**, 1122).

Our new method of formation is to heat the sodium salt of Schaeffer's β-naphtholmonosulphonic acid in a metal retort, platinum or copper, to low redness. The distillate condenses almost immediately to a yellowish solid. The total yield from the dry sodium salt is considerable, but was not determined quantitatively; the main portion of this distillate was found to consist of I, β-naphthol; II, β-dinaphthyl ether; and III, dinaphthylene oxide. To separate these three compounds, the distillate was first treated with dilute sodium hydrate solution, in which about 50 per cent. dissolved, and on acidifying the alkaline solution, a very pure β-naphthol, melting at 122°, was precipitated. Little else appeared to have been dissolved. The portion insoluble in soda was then boiled with glacial acetic acid, in which it dissolved completely, and, on slightly cooling, a yellow, fluorescent substance crystallised out, which, on recrystallisation from acetic acid, formed very fine, rhombic plates melting at 153°.

Analysis:—

0·1850 gram substance gave 0·6080 gram CO_2, and 0·0755 gram H_2O.

	Found.	Theory.
C_{20}........	89·62 per cent.	89·55 per cent.
H_{12}........	4·53 ,,	4·48 ,,
O.........	— ,,	5·97 ,,

With picric acid in alcoholic solution, a compound is formed which melts at 134°. It forms groups of dark-red needles.

The acetic acid solution evaporated to some extent, on cooling, gave colourless crystals of a substance of low melting point, which, on recrystallisation from dilute alcohol, was obtained in bright, silky plates melting at 105°.

The analysis of this substance and its physical properties show it to be dinaphthyl ether.

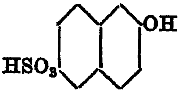
0·2010 gram substance gave 0·8536 gram CO_2 and 0·0350 gram H_2O.

	Found.	Theory.
C_{20}........	88·67 per cent.	88·88 per cent.
H_{14}........	5·25 ,,	5·18 ,,
O.........	— ,,	5·94 ,,

The yield of dinaphthylether thus obtained is between 4 and 5 per cent., and that of dinaphthylene oxide about 25 per cent. of the total crude distillate.

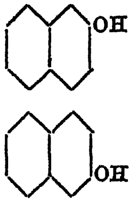
The dinaphthylene oxide agrees in all its properties with the compound described by Knecht and Unzeitig (*Ber.*, **13**, 1724, and (*Annalen*, **209**, 138). It melts at 153°, and boils without any decomposition at a temperature close upon, if not above, 500°.

This method of formation of dinaphthylene oxide from Schaeffer's β-naphtholmonosulphonic acid points quite clearly to its constitution.

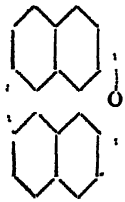
Schaeffer's acid has the constitution  .

The sodium salt of this acid when heated gives sodium sulphite. The two residues unite to form dinaphthol and dinaphthylene oxide respectively.

As a matter of fact, dinaphthol does exist amongst the products of the distillation, but only in very small quantity, for, as might be expected, the high temperature at which the reaction takes place causes the elimination of water and formation of dinaphthylene oxide.



Dinaphthol.



Dinaphthylene oxide.

Dinaphthylene oxide is easily sulphonated, either by warming with ordinary strong sulphuric acid, or by dissolving in chloroform and treating with sulphuric acid mixed with 80 per cent. of the anhydride; or by the action of sulphonic monochloride, SO_3HCl. As the sulphonation proceeds, the colour changes from blue to brown, and the solution of the acid in water is also brown. The same stage of sulphonation is obtained by all the above mentioned methods, namely, a tetrasulphonic acid.

The barium salt of this acid is very soluble in water when first made, and the solution when filtered through animal charcoal is not fluorescent. After evaporating to dryness, the salt is not quite so soluble in water. When slowly crystallised from the original solution, it contains 10 mols. H_2O, which can be driven off at 120°. The less soluble salt contains but 2 mols. H_2O.

0·1229 salt lost 0·0218 = 17·8 per cent. water at 120°.
0·1056 salt lost 0·0186 = 17·6 „ „ „ (barium lost).
0·2402 „ 0·0412 = 17·1 „ „ „
and gave 0·1070 $BaSO_4$ = 26·2 Ba per cent.

$C_{20}H_8(SO_3)_4Ba_2,10H_2O$ requires 17·6 per cent. water and 26·8 barium.

The ammonium and other salts of this acid have been made, but no particular interest attaches to them.

This sulphonic acid is of interest, because it can be obtained directly from β-naphthol. When β-naphthol is heated with sulphuric acid to a high temperature (120—150°), there is always produced along with the β-naphtholsulphonic acid a certain quantity of sulphonic acid, which does not react with diazo-compounds, and contains therefore no hydroxyl group. The amount of this acid depends on the extent of heating with the sulphuric acid. That these sulphonic acids are derivatives of dinaphthylene oxide can be shown in the following manner:—

The mixture of naphtholsulphonic acids obtained by sulphonating naphthol at a high temperature is made into an alkaline salt, and after the removal of the excess of sulphuric acid with barium carbonate, treated with a diazo-compound. For this purpose diazobenzidine is very convenient, as it forms coloured compounds with all the isomeric naphtholsulphonic acids. These compounds can be precipitated by the addition of salt to their aqueous solutions. The filtrate, which should give no colour reaction on the addition of a little more of the diazo-compound, is somewhat concentrated by evaporation, mixed with an equal bulk of dilute sulphuric acid, and heated in a sealed tube or other closed vessel at a moderately high temperature, 150° or thereabout. By this means all the sulphonic groups are eliminated, and the dinaphthylene oxide separated in a crystalline form. After one or two crystallisations from acetic acid, it is obtained quite pure of m. p. 153°, and is otherwise also identical with the product from Schaeffer's acid above mentioned.

This process can even be watched, as the β-naphtholtrisulphonic acid is gradually converted into dinaphthylene oxide tetrasulphonic acid:—

1. By analysis at different stages of heating, when it is observed

that both the sulphur and the barium (in the barium salt) diminish in amount.

2. By the difference in the colour of the fluorescence of the acid solution, the green fluorescence of the trisulphonic acids passing into blue as the dinaphthylene oxide acids are formed.

3. In a more definite manner by heating naphthol with five times its weight of slightly fuming sulphuric acid quickly to 120—130°, and keeping it at that temperature for one hour. It is then converted completely into the trisulphonic acid. Small weighed quantities of this are taken, rendered alkaline, and titrated with a solution of diazobenzidine of known strength, as long as the colouring matter is formed. From the amount of diazobenzidine solution used, the quantity of the trisulphonic acid can be calculated. If the heating be continued past this stage, sulphur dioxide is formed, and the amount of trisulphonic acid regularly diminishes. This can also be watched by taking analyses at different stages.

An analysis of the barium salt of a portion immediately after the stage of formation of the trisulphonic acid gave Ba 34·85 per cent. and S 16·15 per cent.

Barium β-naphtholtrisulphonate requires Ba 35·04 per cent. and S 16·37 per cent.

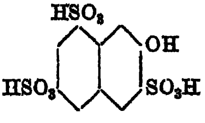
After several hours continued heating at 140—150°, an analysis of a barium salt gave considerably less barium: Ba 32·6 per cent. and S 14·8 per cent.

Barium dinaphthylene oxide tetrasulphonate, $C_{20}H_8(SO_3)_4Ba_2$, dried at 120°, requires Ba 32·54 per cent. and S 15·2 per cent.

It would appear, therefore, that in this action, as in the distillation of the sodium salt first mentioned, the SO_3 groups in the para-position relatively to the hydroxyl are successively removed with simultaneous joining up of the two naphthol rings.

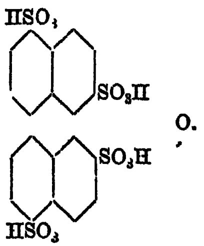
The constitution of this tetrasulphonic acid is also clear from the fact that all the isomeric mono- or di-sulphonic acids of β-naphthol give one and the same trisulphonic acid on further, somewhat drastic, treatment with sulphuric acid; (Limpach, *Ber.*, **16**, 726); see also Nietzki (*Chem. Zeit.*, **15**, 296; also *Jour. Chem. Ind.*, **10**, 6, 536).

As this acid must have the constitution



,

the only possible constitution for dinaphthylene oxide tetrasulphonic acid is



Dinaphthylene oxide is brominated tolerably easily either in acetic or chloroform solution; with a large excess of bromine, a product was obtained crystallising in very slender needles, and almost colourless; it melts at 231°.

On analysis. 0·2578 gram substance gave 0·3353 gram AgBr, or 55·35 per cent. of bromine.

The formula $C_{10}H_8Br_4O$ requires 55·17 Br. It is therefore a tetrabromo-derivative. When less bromine is employed, evidently some lower brominated derivatives are formed; these have lower melting points than the one mentioned, but were not examined further. Chlorine in large excess acting on dinaphthylene oxide in chloroform solution gives a chlorine derivative of similar appearance to the bromine one. It melts at 220°.

Dinaphthylene oxide dissolves in glacial acetic acid very easily, and on adding strong nitric acid to this solution without heating, a nitro-derivative is precipitated in fine, red needles, melting at 185°.

0·2658 gram substance gave 10·3 c.c. N at 763 mm. and 17·4° = 4·47 per cent. N; $C_{20}H_{11}NO_3$ requires 4·47 per cent. of nitrogen.

Attempts to reduce this substance have not as yet been successful. On boiling with strong nitric acid for a little time the nitro-derivative dissolved, and on cooling separated in crystals not very distinct in shape. It was washed with hot acetic acid, dried, and analysed.

0·1264 gram substance gave 13·9 c.c. N at 755·2 mm. and 18°, or 12·5 per cent. nitrogen.

0·1036 gram substance gave 11·4 c.c. N at 754 mm. and 17°, or 12·66 per cent. nitrogen.

$C_{20}H_8N_4O_9$ requires 12·5 per cent. nitrogen.

It is therefore a tetranitro-derivative. This compound begins to melt at about 250°, but decomposes at the same time.

The mononitro-derivative, when treated with excess of bromine, gives a yellow bromonitro-derivative forming rhombic prisms, somewhat resembling nailhead spar in appearance. It melts at 295°.

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ERRATA.

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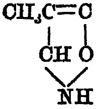
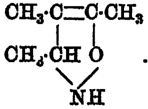
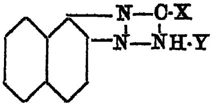
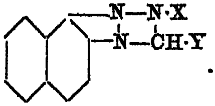
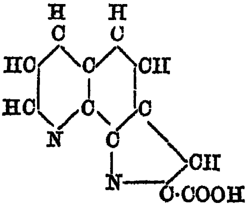
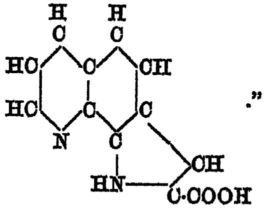
51	15	from bottom *et seq.*, *for* "In the paper . . . on the subject," *read* "In this paper, Dunstan and Dymond discuss my own experiments on the subject, the account of which was published in abstract only (*Proc. Chem. Soc.*, 1889, 134)."
318		Figures 2 and 3 on this page are placed upside down, so that the obtuse axial angle is at the lower part of the crystal instead of the upper part, as stated in the context.
426	10	from top, *for* "  " *read* "  ."
533	9	„ „ *for* " through *y*" *read* " through *g*."
533	3	„ bottom, *for* " 0·2922" *read* " 0·2992."
534	5	„ top „ " (ignited)...... 0·44" *read* " (ignited)...... 0·15."
680		bottom, *for* "  " *read* "  ."
759	14	from top, *for* "  " *read* "  ."
759	17	from top, *for* " $C_{12}H_7N_2O_2$" *read* " $C_{12}H_8N_2O_2$."

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